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Synthesis, characterization, and reactivity of sulfided hexanuclear molybdenum cluster compounds

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Synthesis, characterization, and reactivity of sulfided hexanuclear molybdenum cluster compounds

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DEDICATION

This dissertation is dedicated to the memory of my brother, Jeff. I am thankful for his pride in me and sorry that he could not see the end results of my studies. I regret that he did not get the chance to go back to school to finish his own studies so that I could reciprocate the support.

GENERAL INTRODUCTION

Statement of the Problem

The existence of hexanuclear molybdenum clusters was first established by Brosset in 1945 [1]. They are known to exist in molybdenum(II) halides [2], as well as the ternary molybdenum chalcogenides known as Chevrel phases, $M_xMo_6Y_8$ (M = ternary metal cation; Y = chalcogenide) [3,4]. Many Chevrel phase compounds have been found to be superconductors [5], show catalytic activity [6], and finally, are ionic conductors [7], thus raising considerable interest in these compounds.

Although the overall structures of these two classes of compounds are very different, the similarities between the clusters have led to the investigation of a series of mixed halide-chalcogenide clusters, $[Mo_6Y_xX_{8-x}]$ (X = halide; Y = chalcogenide). Members of the series with x = 1 in $Mo_6Cl_{10}Y$ (Y = S, Se, or Te) [8], x = 3 in $Mo_6Br_8S_2$ [9], x = 4 in $Mo_6Br_6S_3$ [10], and x = 6 in $Mo_6S_6X_2$ (X = Br, I) [11,12], have been synthesized. The actual stoichiometries of the clusters are not necessarily reflected by the formulas because of the sharing of ligands between clusters in the structures. All of these have structures related to the Chevrel phases. The structures of these cluster compounds will be discussed further, *vide infra*.

Additional work has also been done in the investigation of a series of molecular clusters with mixed halogen and chalcogen ligands [13-16]. Michel and McCarley reported the first molecular Mo_6X_8 cluster compound with mixed bridging ligands, $(pyH)_3[(Mo_6Cl_7S)Cl_6]$ [13]. Other molecular mixed halide-chalcogenide clusters have also been reported for x = 5, 6, and 7 in the form $Mo_6S_xCl_{8-x}{\cdot}npy$ (py =

pyridine; n = 3, 6, or 5 when x = 5, 6, or 7 respectively) [14]. Additional members of the series, $Mo_6Cl_{(8-x)}S_x \cdot 6L$, where x varies from 4 to 8, have also been studied, but are less well characterized [15,16]. In these studies, the terminal ligand, L, was pyridine, *n*-propylamine, a trialkylphosphine, or other coordinating ligand. The results suggested that the products of these attempted preparations were not single stoichiometric clusters, but rather, were mixtures of cluster products which had a range of values of x.

The binary Chevrel compound, Mo_6S_8, is a metastable compound and its synthesis is achieved only by indirect methods. A ternary phase must first be prepared by typical high temperature methods and the ternary metal, usually Cu or Ni, subsequently removed by oxidation with acid [17]. The preparation of metastable compounds through low temperature routes *via* molecular precursors has received a good deal of attention in recent years [18,19]. A potential application of the preparation of molecular Mo_6S_8 clusters would be to use these cluster compounds as soluble precursors to the Chevrel phase compounds.

As part of the overall goal of preparing a molecular compound of the type $Mo_6S_8 \cdot 6L$ which could be used as a precursor to Chevrel phase materials, the specific purpose of much of the research discussed herein was to further investigate the synthesis and properties of the mixed sulfide chloride clusters, $[Mo_6S_xCl_{(8-x)}] \cdot 6L$ ($4 \leq x \leq 8$). It was hoped that a better understanding of the properties of this series of compounds would provide a basis for further study of the reactivity of the end member of the series, $Mo_6S_8 \cdot 6L$. Separation of the sulfur substituted clusters with

$4 \leq x \leq 8$ from one another was pursued to aid in more complete characterization of these compounds.

If there is to be any application for molecular $Mo_6S_8 \cdot 6L$ cluster compounds as precursor materials, it is necessary to know about the reactivity of such species. To that extent, investigation of ligand substitutions and possible ligand removal of several $Mo_6S_8 \cdot 6L$ compounds was undertaken.

Structures

The structure of an Mo_6X_8 cluster is shown in Figure 1. The cluster can be considered as an octahedron of molybdenum atoms with eight triply bridging ligands that cap each face to form a cube. These bridging ligands are noted by Schäfer as "i" for "inner" [20]. An additional set of six ligands occupies the coordination positions found at each vertex of the octahedron. In Schäfer's nomenclature system these are noted as "a" for "ausser". Thus, each octahedron of molybdenum atoms is coordinated by a total of fourteen ligands.

The ligands can be shared between clusters in various ways to give a variety of structures. Using Schäfer's terminology, the connectivities are a-a, a-i, and i-i. For example, an a-a designation denotes a ligand in the terminal position of one cluster which is shared through a terminal position of another cluster. The possible connectivities are demonstrated in Figure 2. By utilizing different combinations of these connectivities, compounds can take on various stoichiometries which can lead to a wide variety of chemical and physical properties.

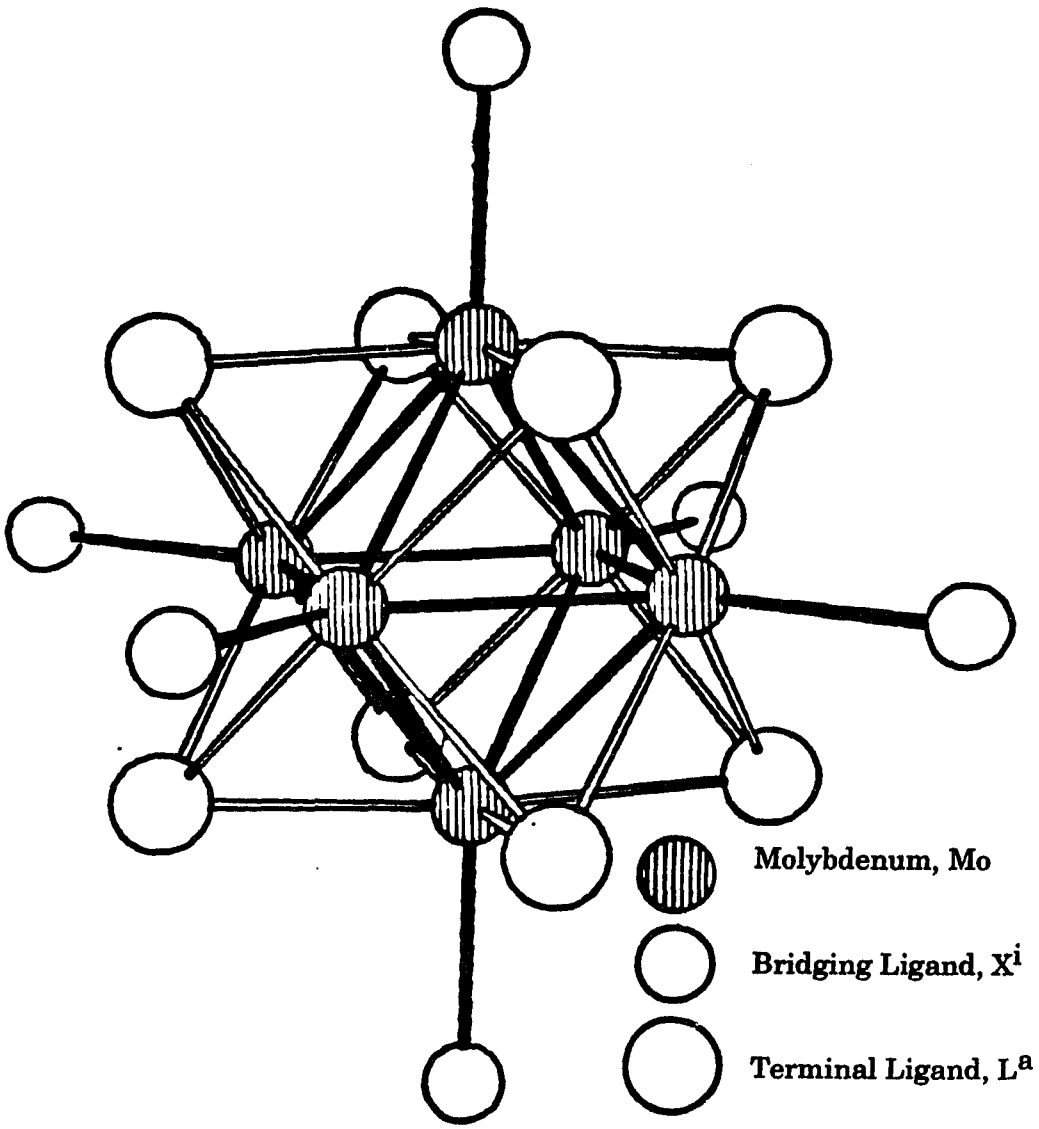


Figure 1. The $Mo_6X^i_8L^a_6$ cluster

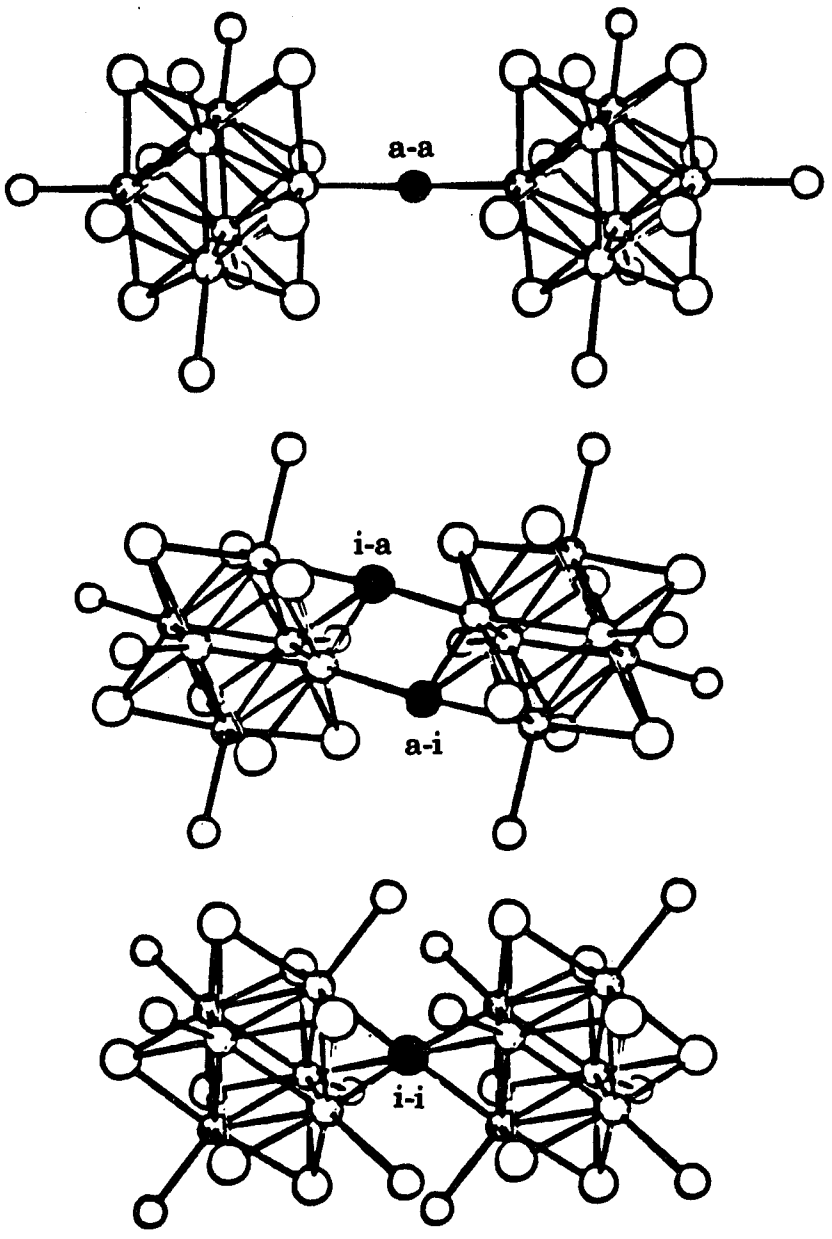


Figure 2. Possible ways that ligands can be shared between Mo_6X_8 clusters

Molecular cluster compounds

Discrete Mo_6X_8 (X = halide) units were first found in the molybdenum(II) compound, $Mo_6Cl_8(OH)_4 \cdot 14H_2O$ by Brosset [1]. Other molybdenum halides having such cluster units were thoroughly investigated by Schäfer and von Schnering [20]. As a specific example, in α-$MoCl_2$, $Mo_6Cl_8^{4+}$ clusters are joined together by the sharing of terminal chlorides between the cluster units as indicated by the formula $(Mo_6Cl_8^i)Cl_2^aCl_{4/2}^{a-a}$. Such connectivity results in separation of the octahedral clusters by 4.54Å. This is the nearest intercluster molybdenum-molybdenum distance and is far beyond the range of any bonding interaction. Consequently, the clusters can be considered as discrete, non-interacting units. The cluster units in the halides can be completely independent from one another when additional coordinating ligands are present to occupy the terminal positions, as in $(Mo_6X_8)X_4L_2$ [21].

Molecular chalcohalides As it has been used in the literature, the term "chalcohalide" will be used here to refer to a cluster compound with mixed halide-chalcogenide bridging ligands of the sort $Mo_6X_{8-x}Y_x$. The chalcohalide clusters discussed here, for which crystal structures have been solved, contain discrete, non-interacting clusters. The terminal ligands are either chlorides or coordinated organic ligands.

The first report of a molecular chalcohalide was made by Michel and McCarley [13]. The $Mo_6SCl_7^{3+}$ cluster was found as the product of the reaction between Mo_6Cl_{12} and two equivalents of NaSH. It was isolated in the structures $(pyH)_3[(Mo_6SCl_7)Cl_6]$ and $(pyH)_3[(Mo_6SCl_7)Cl_6] \cdot 3pyHCl$ (py = pyridine). The sulfur and chlorine positions were indistinguishable by x-ray diffraction structure solving

techniques. X-ray photoelectron spectroscopy confirmed that the sulfide occupies a bridging position of the cluster and not a terminal position. The cluster anions are isostructural with the $(Mo_6Cl_8)Cl_6^{2-}$ cluster found in $Hg[(Mo_6Cl_8)Cl_6]$, for example [22].

The crystal structure of a compound whose composition was thought to be $Mo_6S_6Cl_2 \cdot 6py$ was also reported by Michel [14]. Again, structural data provided no evidence for an ordering of the sulfides and chlorides in the bridging positions of the cluster. Materials with the compositions $Mo_6S_5Cl_3 \cdot 3py$ and $Mo_6S_7Cl \cdot 5py$ were also found and gave the same or very similar x-ray powder patterns as $Mo_6S_6Cl_2 \cdot 6py$. The average Mo-Mo bond length in $Mo_6S_6Cl_2 \cdot 6py$ is 2.634Å, approximately 0.02Å longer than the distances found in Mo_6Cl_{12}, or the $(Mo_6SCl_7)Cl_6^{3-}$ cluster.

Recently, a molecular $Mo_6S_8 \cdot 6L$ cluster compound was achieved [23]. In this case, the six terminal positions were filled by triethylphosphine ligands. Consequently, these were discrete molecular clusters with no intercluster metal-metal interactions. Simultaneously, Japanese researchers reported the synthesis of the same cluster using a different procedure [24]. The same average intracluster Mo-Mo bond distance of 2.66Å was found by both sets of workers.

Lengthening of the metal-metal bond most likely results from oxidation of the cluster and removal of electrons from metal-metal bonding orbitals. The experimental results are in fairly good agreement with predicted bond lengths. Based on bond order considerations, the bond length change expected when going from Mo(II) (24 cluster electrons), to an average oxidation state of +2.33 (22 cluster electrons), is 0.023Å, and further oxidation to an average oxidation state of +2.67 (20

cluster electrons), should result in a lengthening of the bond by 0.048Å [25]. These values are consistent with the observed bond lengths in $Mo_6S_6Cl_2 \cdot 6py$ and $Mo_6S_8 \cdot 6PEt_3$.

Chevrel phases and related solid state materials

In the Chevrel phases, MMo_6Y_8 (M = Pb, Sn, and many others; Y = chalcogenide) [26], the clusters are linked together resulting in strong metal-metal interactions between the cluster units. The connectivity in these compounds can be written as $(Mo_6S_2^iS_{6/2}^{i-a})S_{6/2}^{a-i}$, and is shown in Figure 3. This connectivity results in close approach of the cluster units. For example, in $PbMo_6S_8$, 3.270Å is the shortest intercluster Mo-Mo distance.

Chalcohalides The variety of structures available through utilization of variations of linkages between clusters is exemplified by the structures of these chalcohalides. Discrete molecular clusters as well as strongly interacting clusters are known. The molecular species have already been covered and this section will focus on the solid state structures. These compounds will be discussed in order of increasing amount of ligand sharing. Recent reviews by Perrin and Sergent also provide excellent coverage of these compounds [27,28].

The structures of $Mo_6Cl_{10}Y$ (Y = S, Se, Te), are isomorphous with the Nb_6I_{11} structure and can be described by the formulation $(Mo_6Cl_7Y)Cl_{6/2}^{a-a}$ [8]. The chalcogen and halogen atoms are disordered in the bridging positions. The average intracluster Mo-Mo distance is 2.616Å and the nearest intercluster Mo-Mo distance is 4.4Å.

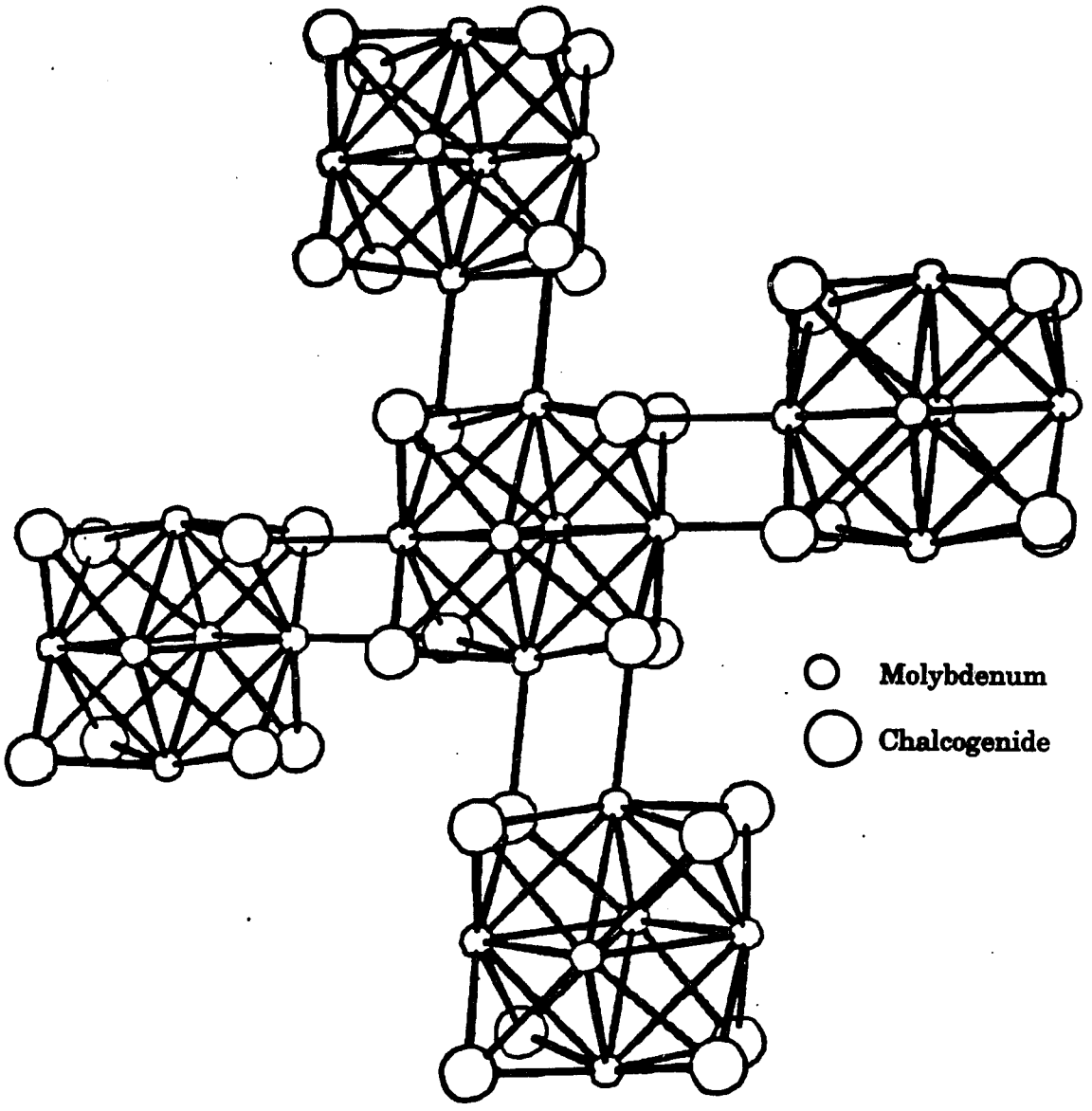


Figure 3. Structure of the Chevrel phases showing four of the six neighboring clusters

$Mo_6X_8Y_2$ (X = Br, Y = S; X = I, Y = S, Se), compounds show a great deal of ligand sharing to give one-dimensional chains [9]. The compounds have an $Mo_6X_5Y_3$ cluster core and are formulated $(Mo_6Br_5^{i}S^{i}S_{2/2}^{i-i})Br_{6/2}^{a-a}$. All of the compounds in this group are isostructural, based on x-ray diffraction powder data. However, single crystals suitable for structure determination were obtained only for $Mo_6I_8Se_2$. The intracluster and intercluster Mo-Mo distances in this compound were determined to be 2.71Å and 3.92Å, respectively.

$Mo_6Br_6S_3$ offers an example of a $Mo_6Y_4X_4$ cluster [10]. Its structure is only slightly different from $Mo_6I_8Se_2$. Additional ligands are shared through i-a linkages. The formulation is $(Mo_6S_{2/2}^{i-i}S_{2/2}^{i-a}Br_4^{i})Br_{4/2}^{a-a}S_{2/2}^{a-i}$. An intercluster Mo-Mo approach of only 3.53Å is found in this layered compound.

Chalcohalides with the Chevrel phase structure are found in $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ [11,12]. The halogens in these structures replace the chalcogens on the unique 3-fold axis of the cluster in the Chevrel phases. The structure is described by the formulation $(Mo_6S_{6/2}^{i-a}Br_2^{i})S_{6/2}^{a-i}$. The intercluster Mo-Mo distance in this compound is 3.225Å which is shorter than that of $PbMo_6S_8$.

It is interesting to note that when the chalcogenide in the cluster is sulfide, the halide is most often bromide or iodide. The only solid state chloride sulfide cluster is $Mo_6Cl_{10}S$. French researchers have attributed this to the smaller size of these two atoms. "$Mo_6S_6Cl_2$" would require too great a distortion of the cluster [26]. They also noted that the larger atoms seem to have a stabilizing effect on these clusters [11]. An overview of some of the structural features of these cluster compounds is given in Table I.

Table I. Survey of compounds containing Mo_6X_8 clusters

Formula	Structural Formula	$[Mo_6X_8]$ Core	Cluster Electrons[a]	d(Mo-Mo)[b] (intra)	d(Mo-Mo)[b] (inter)
Mo_6Cl_{12}	$(Mo_6Cl^{i}_{8})Cl^{a}_{2}Cl^{a-a}_{4/2}$	$[Mo_6Cl_8]$	24	2.613	4.54
$[(Mo_6Cl_7S)Cl_6]^{3-}$	$(Mo_6Cl^{i}_{7}S^{i})Cl^{a}_{6}$	$[Mo_6Cl_7S]$	24	2.61	
$Mo_6Cl_{10}S$	$(Mo_6Cl_7S)Cl^{a-a}_{6/2}$	$[Mo_6Cl_7S]$	24	2.60-2.63	4.4-4.8
$Mo_6I_8Se_2$	$(Mo_6I^{i}_{5}Se^{i}Se^{i-i}_{2/2})I^{a-a}_{6/2}$	$[Mo_6I_5Se_3]$	24	2.71	3.92
$Mo_6Br_6S_3$	$(Mo_6S^{i-i}_{2/2}S^{i-a}_{2/2}Br^{i}_{4})Br^{a-a}_{4/2}S^{a-i}_{2/2}$	$[Mo_6Br_4S_4]$	24	2.63-2.68	3.53-3.54
$Mo_6S_6Br_2$	$(Mo_6S^{i-a}_{6/2}Br^{i}_{2})S^{a-i}_{6/2}$	$[Mo_6Br_2S_6]$	22	2.72-2.73	3.225
$PbMo_6S_8$	$(Mo_6S^{i-a}_{6/2}S^{i}_{2})S^{a-i}_{6/2}$	$[Mo_6S_8]$	22	2.705	3.270
Mo_6S_8	$(Mo_6S^{i-a}_{6/2}S^{i}_{2})S^{a-i}_{6/2}$	$[Mo_6S_8]$	20	2.780	3.085
$Mo_6S_8 \cdot 6PEt_3$	$(Mo_6S^{i}_{8})L^{a}_{6}$	$[Mo_6S_8]$	20	2.66	

[a]This is the total number of metal valence electrons per Mo_6 unit.
[b]Distances in Angstroms.

Electronic Structures

Molybdenum(II) halides

The electronic structure of the clusters in molybdenum(II) halides has been discussed extensively [29-31]. The Xα calculations of Cotton and Stanley [31] showed that the highest occupied metal-metal bonding orbital is of E_g character, which is in agreement with the earlier more simple calculations. The molybdenum cluster can be viewed as having twenty-four electrons (four from each metal atom), in twelve orbitals of primarily metal-metal bonding character. Thus, the metal-metal bonding within the cluster can be described as twelve single bonds, one along each of the edges of the octahedron. This is supported by an average Mo-Mo bond distance of 2.613Å [20], which is what is expected from bond order-bond length considerations using bcc metallic molybdenum, (2.614Å) [32]. The calculations are in good agreement with spectroscopic data [21,33].

Chevrel phases

The electronic structure of the Chevrel phases has also been extensively studied [34-38]. Only the general features of the calculated band structures will be discussed here.

The first band structure calculation on Chevrel phase compounds was reported by Andersen *et al.* [34]. They used the linearized muffin-tin orbital (LMTO) approach and the atomic sphere approximation. They found the conduction band to be of primarily e_g character and located just below the 24 electron gap. This is in fairly

good agreement with the simple molecular calculations on the cluster discussed above.

The conduction band is fairly localized on the metal atoms to give a sharp peak in the density of states curve. The shape of this band explains the superconducting behavior of the compounds with less than 24 electrons. More recent calculations [35-38] confirm the basic results found in the earlier reports.

The similarities between the electronic structures of the Mo_6X_8 clusters in molecular compounds and those with intercluster bonding can be seen in this brief discussion. Further discussions and comparisons have been presented in the literature [37,38].

Chemical and Physical Properties

As mentioned briefly above, it is the properties of the Chevrel phase materials which make them interesting. Because of potential applications of their properties, new, more efficient routes to their preparation in bulk are being investigated, as well as the preparation of useful devices such as thin films. It is therefore worthwhile to review the properties of the Chevrel phases as well as the molecular compounds used in this research.

Molecular compounds

Because the molybdenum(II) halides have been known for a long time, a great deal is known about their reactivity and other chemical properties. The discussion

here will focus primarily on Mo_6Cl_{12} since it was used as a starting material for the substitution studies done in this work.

The metal cluster itself is actually quite robust. The hexanuclear unit remains intact even in boiling aqua regia or fuming sulfuric acid [21]. It does however decompose in strongly basic solutions. The majority of the reactivity of these compounds occurs as ligand substitution.

Formation of adducts The availability of six terminal coordination sites allows for neutral ligands to form adducts with the Mo_6Cl_{12} cluster of the type $(Mo_6Cl_8)Cl_4L_2$. Bis adducts are formed with a number of coordinating ligands such as pyridine, triethylamine, tri-*n*-propylphosphine, tri-*n*-butylphosphine, tri-*n*-pentylphosphine [33,39]. Other phosphine derivatives may also be formed. Triphenylphosphine and diphenylethylphosphine will form adducts with the cluster, but with triethylphosphine or diethylphenylphosphine reduction was found to occur [40]. The cluster was also reduced by tri-*n*-propylphosphine in these latter experiments, in contrast to the result claimed above.

Substitution at L^a sites The outer ligands, Cl^a, in $[Mo_6Cl_8^i]Cl_4^a$ can be replaced by other halides or pseudohalides. When reacted with the hydrohalic acids at 200 to 250°C *in vacuo*, $Mo_6Cl_8X_4$ results (X = Br, I) [33,41]. When X is fluorine, incomplete substitution occurs. Halide substitution occurs in the outer ligand positions when the cluster is reacted with mercuric halide salts as well [42].

Fluoride ions will also replace Cl^a. Reaction of Mo_6Cl_{12} with aqueous ammonium fluoride results in the replacement of the four outer chloride ligands by three fluoride and a hydroxide ligand. By reaction of these two reagents in

methanol, the ammonium salt of the fluoroanion is achieved, $(NH_4)_2[Mo_6Cl_8]F_6$. The cesium salt is prepared analogously [43].

The cluster can also be hydrolyzed to give hydroxide ligands in these terminal positions [33]. Methoxide can also occupy these positions [43,44]. Finally, it has also been shown that alkyl groups can be substituted into the outer coordination positions [39].

<u>Substitution at X^i sites</u> The $Mo_6Cl_8^{4+}$ cluster is inert to aqueous halide [33] but will react with molten lithium salts at high temperature as described in equation (1) below [45].

$$Mo_6Cl_{12} + 12\ LiX \longrightarrow Mo_6X_{12} + 12\ LiCl \qquad (1)$$

$$(X = Br, I)$$

For clusters, $Mo_6X_8^{4+}$, where X is a halide other than chloride, similar substitution occurs but only by a larger halide. Exchange of X^i for X^a when X^a is the larger also occurs thermally [46].

$$[Mo_6X_8]Y_4 \xrightarrow{200°C} [Mo_6X_4Y_4]X_4 \qquad (2)$$

$$(Y = Br, I \text{ when } X = Cl)$$

In a similar manner, two hydroxide ligands can be inserted into the inner positions.

Replacement of X^i by smaller halides occurs by reaction with mercury(II) halides but only after replacement of the terminal ligands [42]. These reactions are described by (3) and (4).

$$Mo_6X_{12} + 3\ HgY_2 \longrightarrow Hg[Mo_6X_8]Y_6 + 2\ HgX_2 \quad (3)$$

$$Mo_6X_{12} + 7\ HgY_2 \longrightarrow Hg[Mo_6Y_8]Y_6 + 6\ HgX_2 \quad (4)$$

Sulfide ion may also be substituted into the bridging positions. This was first demonstrated by Michel and McCarley [13]. The substitution is believed to proceed by way of an initial substitution of SH^- into a terminal site which then loses a proton and substitutes for an inner chloride. Subsequent efforts have shown that further substitution of up to all 8 bridging ligands by sulfide can occur [23]. A mixed selenide chloride cluster, $[Mo_6SeCl_7]^{3+}$, can be prepared in an analogous manner [47]. Additionally, methoxide is known to replace the inner ligands [44].

<u>Redox chemistry</u> Mo_6Cl_{12} demonstrates both reversible one electron reduction and oxidation waves. A second oxidation is not reversible [48]. Hamer and co-workers showed that the cluster can be chemically reduced with trialkylphosphines (triethyl-, diethylphenyl-, and tri-*n*-propylphosphine). The triethylphosphine derivative was characterized and formulated as $\{[Mo_6Cl_8](PEt_3)_6\}^{2+}\{[Mo_6Cl_8]Cl_6\}^{2-}$ [40]. The result for the tri-*n*-propylphosphine derivative is in disagreement with the results of Saito *et al.* [39].

<u>Physical properties</u> The physical properties of the $[Mo_6X_8]$ cluster compounds are well established and confirm theoretical studies. This discussion will

be very brief and details can be found in the literature. Low temperature electronic spectra confirm that the HOMO and LUMO orbitals of Mo_6Cl_{12} are primarily metal centered [49]. Temperature dependent magnetic susceptibility measurements conclude that the ground state is a closed shell $^1A_{1g}$. Finally, the chloroanion $Mo_6Cl_{14}^{2-}$ is luminescent both in solution and as a solid [49].

Chevrel phases and related solid state compounds

The physical properties of the Chevrel phases are easily explained by their electronic and physical structures. Various aspects of the structures and properties of the Chevrel compounds have been reviewed [4,27,28,50] and only a brief summary will be given here.

Conductivity The Chevrel phases and the related solid state chalcohalides exhibit electrical behavior now understood from theoretical considerations. Species with 24 electrons per Mo_6 cluster unit are insulators or semiconductors, depending on the extent of intercluster interaction. That is, compounds with long intercluster distances like $Mo_6Cl_{10}S$ and $Mo_6Br_8S_2$ are insulators, while $Mo_6Br_6S_3$ is a semiconductor [51], due to narrowing of the band gap with increasing intercluster interaction.

Superconducting transitions occur for species with less than 24 electrons, MMo_6S_8 (M = a variety of ternary metals, including many lanthanides), and $Mo_6S_8X_2$ (X = Br, I). Superconductivity is found to co-exist with magnetic ordering when M is a lanthanide (La, Gd, Lu, Ho, Dy), primarily due to the localization of conduction electrons on the cluster metal atoms [52,53]. High critical fields are also

observed but critical current densities are low. In thin film samples however, improvement is seen in the critical currents [54].

<u>Reactivity</u> The three-dimensional network of Mo_6S_8 units in the Chevrel phases contains channels which allow for the insertion and de-insertion of ternary metal ions. It is the mobility of ions in these channels which allows for the preparation of the metastable binary phase. The ternary phases are oxidized by hydrochloric acid as shown in (5), with the removal of the ternary metal ion [17].

$$M_xMo_6S_8 + 2x\,H^+ \longrightarrow Mo_6S_8 + x\,H_2 + x\,M^{2+} \qquad (5)$$

(M = Ni, Cu, Co, Fe)

Mo_6S_8 can be reduced reversibly by electrochemical methods as well [7]. This is shown in equation (6).

$$x\,M^+ + x\,e^- + Mo_6S_8 \rightleftarrows M_x^+[Mo_6S_8]^{x-} \qquad (6)$$

This intercalation method can also be used to prepare metastable ternary phases [55]. The reversibility of this process may have applications to lithium battery materials [56].

In this research, the stability of the metal cluster of Mo_6Cl_{12} was taken advantage of by substituting sulfide for chloride in the bridging positions of the already formed Mo_6 cluster. The mixed sulfide chloride clusters thus obtained were separated and characterized to better understand the structures and properties of the

series $Mo_6Cl_{(8-x)}S_x$. Further, progress was made toward a better understanding of the reactivity of the molecular species, $Mo_6S_8 \cdot 6PEt_3$, with respect to removal and exchange of the terminal ligands.

PART 1. PREPARATION AND CHARACTERIZATION OF COMPOUNDS CONTAINING HEXANUCLEAR MOLYBDENUM CLUSTERS WITH MIXED SULFIDE AND CHLORIDE LIGANDS, $[Mo_6Cl_{(8-x)}S_x]$, WHERE $4 \lesssim x \lesssim 8$

INTRODUCTION

The occurrence of hexanuclear octahedral clusters of molybdenum which have eight face bridging (μ_3), ligands have been known for many years [1]. The cluster is illustrated in Figure 4. The bridging ligands, X^i, for compounds containing these clusters are usually halides [2] or chalcogenides [3,4], although the occurrence of alkoxides in these positions is also known [57].

The discovery in the early 1970s that many of the chalcogenides, $M_xMo_6S_8$, known as Chevrel phases, were superconductors spurred research in the area significantly. In addition, these materials are also hydrodesulfurization catalysts [6] and ionic conductors [7]. These properties are directly related to the structure of the compounds, which contains a three-dimensional network of clusters.

The clusters found in the Chevrel phases are extremely similar to the well established molybdenum(II) halides. There are also many features of the electronic structures of the two classes of compounds that are analogous [37]. These similarities have brought about interest in the preparation of mixed halide chalcogenide clusters, $[Mo_6X_{8-x}Y_x]$ (X = halide; Y = chalcogenide). Many compounds containing such clusters have been found by Perrin and co-workers [8-12]. Solid-state materials have been synthesized with x = 1 in $Mo_6Cl_{10}Y$ (Y = S, Se, or Te) [8], x = 3 in $Mo_6X_8Y_2$ (X = Br, Y = S; X = I, Y = S, Se) [9], x = 4 in $Mo_6Br_6S_3$ [10], and x = 6 in $Mo_6S_6X_2$ (X = Br, I) [11,12], all of which have structures related to the Chevrel phases. Recent reviews cover the structures of these materials in great detail [27,28].

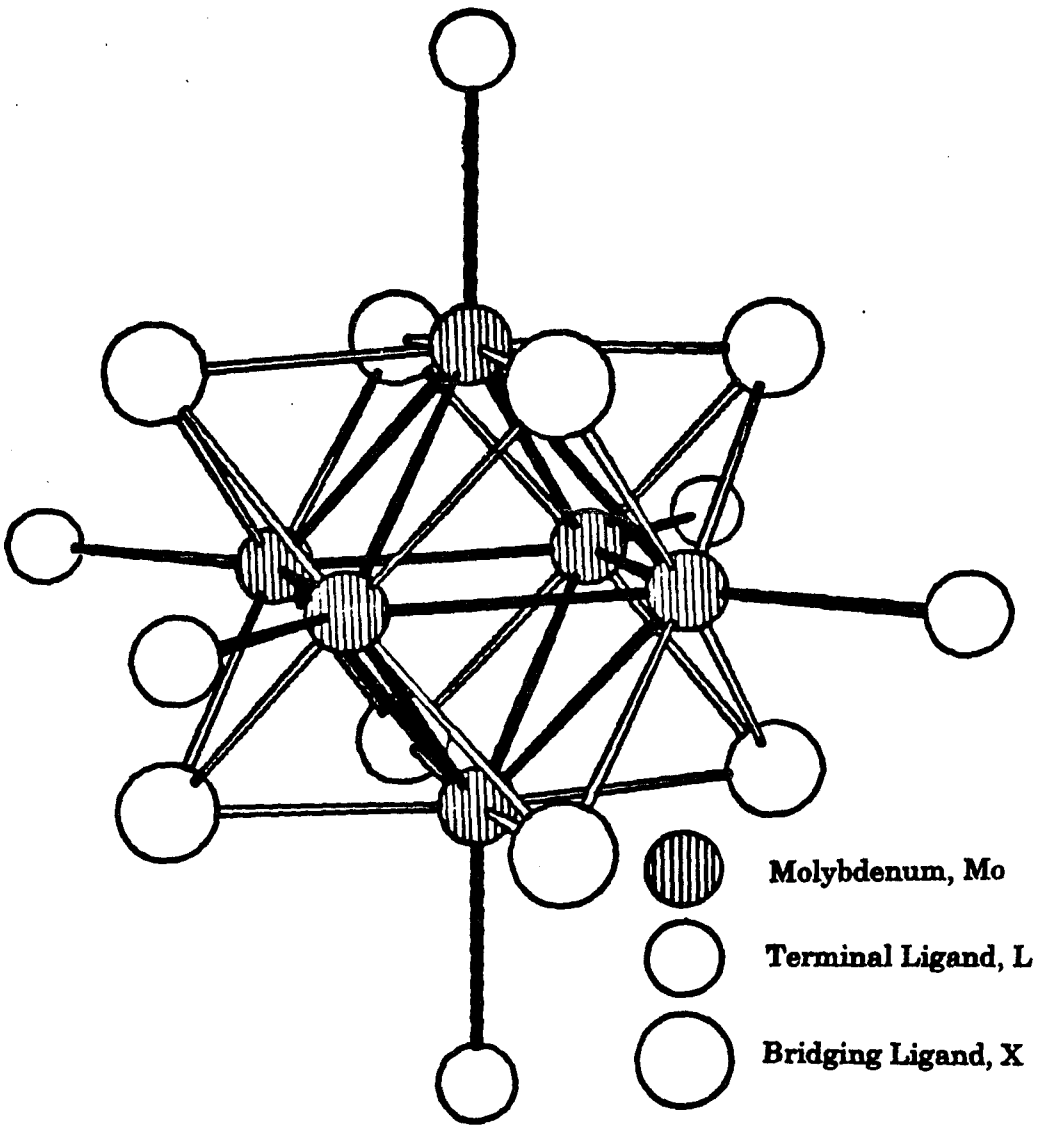


Figure 4. Structure of the $Mo_6X_8L_6$ cluster

Molecular molybdenum halide chalcogenide clusters are not as well known however. $(pyH)_3[(Mo_6Cl_7S)Cl_6]$ and $(pyH)_3[(Mo_6Cl_7S)Cl_6]\cdot 3py$ are the only well established examples [13]. However, with the recent discovery of $Mo_6S_8\cdot 6PEt_3$, the first example of an isolated cluster of molybdenum with sulfide ligands has been established [23,24].

Previous efforts to prepare molecular clusters with mixed ligands have shown that the products are usually mixtures of clusters which are substituted to various extents [15,16]. In an effort to prepare a complete series of molecular clusters, the work reported here investigated the synthesis and properties of the mixed sulfide chloride clusters, $[Mo_6S_xCl_{(8-x)}]L_6$ ($x \approx 4$). Normal phase column chromatography was used to separate the sulfur substituted clusters, $4 \leq x \leq 8$, found in the product mixture.

EXPERIMENTAL

Materials

Reagents

Mo_6Cl_{12}, or α-$MoCl_2$, was prepared by the high temperature conproportionation method described by Koknat *et al.* [58]. Sodium hydrosulfide was prepared by the method described by Brauer [59]. Hydrogen sulfide was bubbled through a solution of sodium ethoxide. The sodium hydrosulfide was recovered by precipitation after addition of ether to the solution. Sodium butoxide was prepared by dissolution of sodium metal in dry butanol. The solution was standardized by hydrolyzing an aliquot and diluting to volume with water. The hydroxide solution was then titrated against standard potassium hydrogen phthalate. The solution was stored under nitrogen and syringed as needed. All solid reagents were stored in a nitrogen atmosphere drybox (dewpoint -75°C). Triethylphosphine was used as obtained from Aldrich Chemical Co. and stored under dry nitrogen.

Solvents

Butanol was dried with sodium metal and subsequently distilled onto outgassed 4Å molecular sieves. Methanol was purified by treatment with either sodium metal or sodium methoxide followed by vacuum distillation onto outgassed 3Å molecular sieves.

Calcium hydride was used to dry pyridine. Following a period of reflux over CaH_2, dry pyridine was obtained by fractional distillation under a steady flow of dry

nitrogen, or by vacuum distillation onto 4Å molecular sieves. Methylene chloride was dried by refluxing over phosphorus pentoxide. This was followed by distillation onto 4Å molecular sieves.

Toluene was refluxed over calcium hydride or phosphorus pentoxide and was distilled onto 4Å molecular sieves to dry. Solvents used for chromatography, cyclohexane, acetonitrile, toluene, and ethanol, were not dried prior to use.

Analytical Procedures

Because many of the materials were pyrophoric in air, samples were prepared for analyses by decomposition in basic aqueous solution under nitrogen. Specifically, samples and vials were removed from the drybox, weighed, then returned to the drybox where the samples were transferred to beakers and covered with a thin plastic film which was secured with a rubber band. After removal from the drybox, an aqueous potassium hydroxide solution was syringed through the film to hydrolyze each sample and the vials were reweighed for tare. Solutions were exposed to air only after samples had been treated with the basic solution. At this point, hydrogen peroxide was added to complete decomposition and oxidation of molybdenum to MoO_4^{2-}.

Molybdenum was determined by precipitation of $MoO_2(ONC_9H_6)_2$ [60]. With this method, the basic solutions were neutralized to a pH = 4 to 6, then buffered with acetic acid/ammonium acetate buffer. The analyte was precipitated by the addition of 8-hydroxyquinoline solution. The solid was filtered through tared filters, washed with hot distilled water, and heated at 140°C overnight to dry.

Chlorine was determined by potentiometric titration of neutralized solutions with standard $AgNO_3$ solution using a Ag/AgCl electrode with a silver electrode as the reference. The endpoint was determined by the second derivative method. Additional microanalyses for molybdenum, chlorine, sulfur, carbon, and hydrogen were obtained from Galbraith Laboratories [61].

Physical Measurements

Infrared spectroscopy

Infrared spectra were obtained from an IR/90 Fourier Transform Infrared Spectrometer made by IBM Instruments, Inc. Samples were prepared as Nujol or paraffin oil mulls. The mulls were pressed between cesium iodide plates to collect data. Reference spectra were obtained using blank cesium iodide plates or air. The sample chamber was constantly purged with nitrogen. Mid-infrared (4000-400 cm^{-1}), and far-infrared (600-200 cm^{-1}), spectra were recorded separately.

Nuclear magnetic resonance spectroscopy

Proton decoupled ^{31}P nmr spectra were collected at 121.05 MHz on WM-200 or WM-300 instruments by Bruker. The instruments were equipped with deuterium lock. Chemical shifts were referenced to 85% phosphoric acid contained in a capillary within the sample tubes.

Samples were put into 10 mm tubes in the drybox. Deuterated solvents, d_6-benzene or d_2-methylene chloride, were syringed from freshly opened bottles into

the tubes through septa. In the sample preparation, exposure to air was minimized but not strictly avoided.

Electron paramagnetic resonance spectra

A Bruker ER200-SRC instrument with an ESR900 cryostat (Oxford Instruments), was used to obtain epr spectra of the compounds discussed here. The nominal frequency was 9.45 GHz and the modulation frequency was 100 kHz. spectra were obtained for all samples at 113K and for some at room temperature. Samples were prepared as methylene chloride solutions in sealed quartz tubes.

Electronic spectra

Electronic spectra were obtained in the region of 200 to 700 nm on a Varian DMS 100S double beam spectrophotometer. Samples were placed in a special sample container in the drybox and solvent was vacuum distilled into the vessel. The solution was filtered into the cuvette of the sample holder and solvent was vacuum distilled from the reservoir to the 10 mm quartz cuvette until an appropriate concentration was achieved. Pure solvent was used as the reference and scan rates of 50 or 100 nm/min were used. At 350 nm and below, a deuterium light source was used.

X-ray powder diffraction

An Enraf Nonius Delft FR552 Guinier camera was used to obtain x-ray powder patterns. A General Electric XRD-5 generator with a Philips normal focus tube and

a Cu target was used to generate the x-rays. Air sensitive samples were ground thoroughly then mounted between strips of cellophane tape in a nitrogen drybox to protect them from air. Powdered NBS silicon was used as an internal standard.

Synthetic Methods

Sulfidation of Mo_6Cl_{12}

The molecular chalcohalide and sulfide clusters were synthesized by substituting sulfur for chlorine in the already formed $Mo_6Cl_8^{4+}$ cluster found in Mo_6Cl_{12}. Sodium hydrosulfide was used as the sulfide source, as in previous substitutions [13]. Sodium butoxide acted in these reactions as a proton acceptor.

Typically, Mo_6Cl_{12} and NaSH were weighed in the drybox and put into a reaction vessel equipped with a reflux condenser. *n*-Butanol was then vacuum distilled into the flask and an appropriate volume of standardized sodium butoxide solution was syringed into the mixture. Excess pyridine was also syringed into the mixture to act as a coordinating ligand to prevent intercluster linkages from being formed during the reaction. The mixtures were stirred under reflux for periods of two to five days.

The resulting pyridine derivatives of the cluster products were extracted with methanol to remove the sodium chloride also formed in these reactions. Analysis: Calc. for $Mo_6Cl_{4.8}S_{3.6}\cdot 4py$: Mo, 48.9%; Cl, 14.4%; S, 9.8%; C, 20.4%; H, 1.7%; N, 4.8%. Found: Mo, 48.6%; Cl, 14.4%; Cl:Mo_6 = 4.8. The purified clusters were then further reacted with triethylphosphine in refluxing toluene. This gave the soluble

triethylphosphine derivatives of the clusters. Analysis: Calc. for $Mo_6S_4Cl_4 \cdot 6PEt_3$: Cl, 9.12%. Calc. for $Mo_6S_5Cl_3 \cdot 6PEt_3$: Cl, 6.86%. Found: Cl, 7.68%.

Unfortunately, the sulfidation reaction described above was non-stoichiometric and resulted in a mixture of cluster products. For this reason, chromatography was employed to separate and isolate the cluster products substituted to different extents.

Chromatography

Chromatographic separations were performed on columns of Celex-N-1 (non-ionic cellulose, Bio-Rad Laboratories), and basic alumina (Bio-Rad Laboratories), which had a water content of 4.623% by weight (determined by weight loss after heating at 180°C for approximately 40 hours). Columns were approximately 30 mm in diameter by 300 mm in length. The solvent reservoir and collection flasks were purged with flowing dry nitrogen during the separations. Eluents were used as obtained from freshly opened bottles. Toluene, cyclohexane, and acetonitrile were obtained from Fischer Scientific.

The product obtained from the reaction with triethylphosphine above was dissolved in cyclohexane and filtered. The solution was transferred by cannula under nitrogen pressure to the Celex-N-1 column. The majority of the material eluted with cyclohexane. This solution was transferred by syringe under nitrogen purge to the basic alumina column. Subsequent elution with increasingly polar (toluene then acetonitrile), and finally hydroxylic (ethanol), solvents achieved good separation of the major products.

Fractions were collected from the point where the dark color of the band began to come off the column until the band was no longer visible on the column. Solids were obtained from each collected fraction by drying *in vacuo*. It is worth noting that when the solid mixture was dissolved in toluene and the same procedure was used, a second band was not isolated from the Celex-N-1 column. Further, $Mo_6S_8 \cdot 6PEt_3$ and the next materials to elute from the basic alumina column were not resolved. However, elution with acetonitrile and ethanol behaved identically in either case. Figure 5 is a schematic description of the procedure.

Isolation of $Mo_6S_8 \cdot 6PEt_3$

This material was separated from the other components by elution from basic alumina with mixed cyclohexane/toluene. This pinkish material was the first to completely elute from the column. Other minor bands moved down the column as well but were not resolved. One of these was green in color which suggested that is was not a hexanuclear molybdenum species. $Mo_6S_8 \cdot 6PEt_3$ was also easily purified by passing solutions containing it through silica gel columns and eluting with toluene. No other bands eluted from the silica gel column. The compound was identified by its far-infrared spectrum.

Isolation of $Mo_6S_{\sim 5}Cl_{\sim 3} \cdot 6PEt_3$

The next band to move down the basic alumina column was eluted with mixed toluene/acetonitrile or acetonitrile (25 to 75 vol%). In either case, only a single band eluted. This material was collected as described above and dried *in vacuo*.

Elemental analyses were obtained from Galbraith Laboratories. Analysis: Calculated for the mixture, $Mo_6S_{5.3}Cl_{2.7}\cdot 6PEt_3$ + 2.5 $S{=}PEt_3$: Mo, 29.89%; Cl, 4.97%; S, 12.98%; C, 31.80%; H, 6.69%; P, 13.67%. Found: Mo, 28.94%; Cl, 4.78%; S, 12.89%; C, 30.87%; H, 6.45%. Mid- and far-infrared spectra and a ^{31}P nmr spectrum were obtained for this fraction.

Isolation of $Mo_6S_4Cl_4\cdot 6OPEt_3$

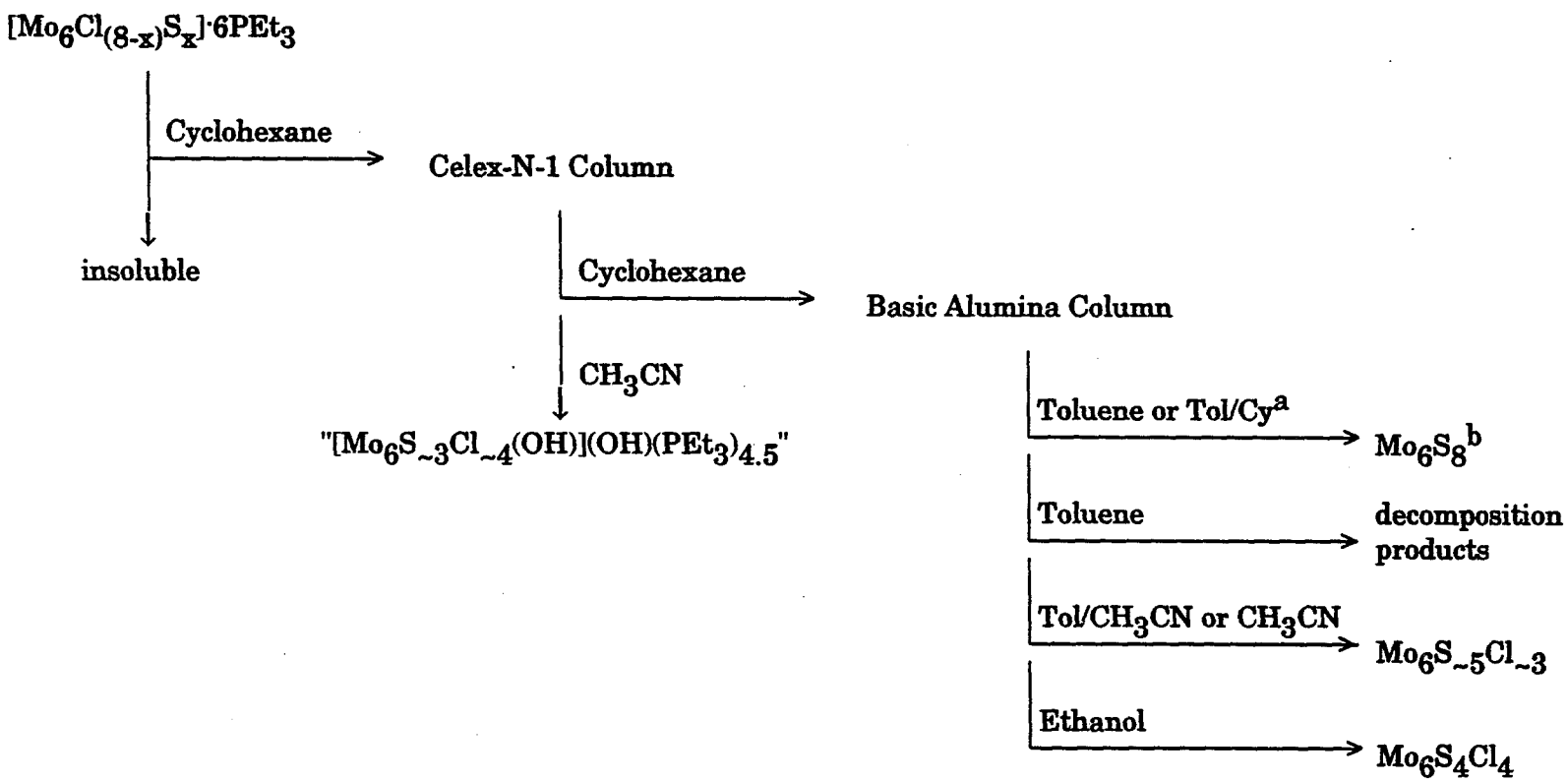
A major band was removed from the basic alumina column by elution with absolute ethanol. Again, it appeared to be a single component band. This material was collected as described above and dried *in vacuo*. Elemental analyses were obtained from Galbraith Laboratories. Analysis: Calc. for $Mo_6S_4Cl_4\cdot 6PEt_3$: Mo, 37.02%; Cl, 9.12%; S, 8.25%; C, 27.81%; H, 5.85%. Calc. for $Mo_6S_4Cl_4\cdot 6OPEt_3$: Mo, 34.87%; Cl, 8.59%; S, 7.77%; C, 26.20%; H, 5.50%; O, 5.82%; P, 11.26%. Found for one sample: Mo, 33.95%; Cl, 8.31%; S, 8.47%; C, 24.80%; H, 5.30%; Cl:Mo_6, 3.97; S:Mo_6, 4.47; C:Mo, 5.84. Found for a different sample: Mo, 27.56%; Cl, 9.58%; S, 6.77%; C, 24.00%; H, 5.08%; Cl:Mo_6, 4.14; S:Mo_6, 4.47; C:Mo, 5.10. Mid- and far-infrared spectra and a ^{31}P nmr spectrum were obtained for the compound.

Approximately 0.5 grams of this material were put into a Schlenk flask. *Ca.* 10 mL of dry methylene chloride were syringed into the flask under nitrogen flow. The solution was then placed in the refrigerator. After about 2 weeks, crystal growth was observed. However, the size of the crystals was only about 0.05 mm x 0.05 mm x 0.05 mm and crystallinity was lost upon removal of the solvent. No further work was done with this material.

In an effort to prepare the triethylphosphine derivative from the triethylphosphine oxide derivative obtained from the chromatographic separation, a small sample, *ca.* 50 mg, of the ethanol eluted product was mixed with 2 mL PEt_3 and 20 mL of dry toluene. The mixture was stirred and brought to reflux for 24 hours. Initially, solubility was only slight but upon filtering the products, no solid was recovered. The solvent was evaporated to near dryness then layered with ethyl ether which caused a precipitate to form. This solid was washed twice with 5 to 10 mL dry ethyl ether. The materials were then dried leaving a brown microcrystalline product in the ether insoluble fraction and colorless needles in the ether soluble fraction. Infrared spectra were obtained for both products and an x-ray powder pattern was also obtained for the cluster product.

Isolation of the second fraction from the Celex-N-1 column

The final isolated band was eluted from the Celex-N-1 column with acetonitrile. The solution collected under nitrogen purge was dried *in vacuo*. Elemental analyses were obtained from Galbraith Laboratories. Analysis: Calc. for $Mo_6Cl_{4.6}S_3(OH)_{1.4}(PEt_3)_{4.5}$: Mo, 41.4%; Cl, 11.7%; S, 6.9%; C, 23.3%; H, 5.0%; O, 1.6%; P, 10.0%. Found: Mo, 38.64%; Cl, 10.99%; S, 6.76%; C, 21.54%; H, 4.55%; Cl:Mo_6, 4.6; S:Mo_6, 3.1; C:Mo, 4.5. Mid- and far-infrared spectra and ^{31}P nmr spectra were obtained for the compound. Isolation of this fraction was not reproducible.



[a]Tol = toluene, Cy = cyclohexane.

[b]Products eluted from the basic alumina column are presumed to be the (hexakis)triethylphosphine derivatives. The formulas are incomplete for the sake of simplicity.

Figure 5. Scheme showing the chromatographic separation of $Mo_6Cl_{(8-x)}S_x \cdot 6PEt_3$

RESULTS AND DISCUSSION

Syntheses

It has been shown, from the results of this work and that of other workers [13-15], that sodium hydrosulfide is effective in sulfiding the $[Mo_6Cl_8]$ cluster. However, as with previous approaches, the sulfidation was found to be non-stoichiometric, even when base was added to the reaction mixture. A distribution of sulfided cluster compounds, $Mo_6Cl_{(8-x)}S_x$, was achieved.

In the initial sulfidation step, described by equation (7), a pyridine derivative, $Mo_6Cl_{(8-x)}S_x \cdot npy$, was obtained where $x \approx 3.6$ and $n \approx 4$.

$$Mo_6Cl_{12} + 4\,NaSH + 4\,NaOBu \xrightarrow[\text{BuOH, 118°C}]{\text{py (xs)}} Mo_6Cl_{(8-x)}S_x \cdot npy + 8\,NaCl + 4\,BuOH \qquad (7)$$

At this point the product was pyrophoric. The incomplete ligation of the cluster ($n < 6$), accounts for this high reactivity. The extent of the sulfide substitution was somewhat lower than the reaction stoichiometry. The molybdenum and chlorine analyses suggested an average of 3.6 sulfides per cluster, not 4. Because sodium chloride was a co-product of the reaction, incomplete extraction with methanol to remove this product may account for the higher than expected chlorine analysis. It should be noted however, that when the reaction stoichiometry is increased to 8 equivalents of sodium hydrosulfide per cluster, the resulting product still contains approximately one chloride per cluster [15].

After purification and further reaction with triethylphosphine as in equation (8), the soluble product had a chlorine content which fit $Mo_6Cl_{(8-x)}S_x \cdot 6PEt_3$, where $x \approx 4.6$.

$$Mo_6Cl_{(8-x)}S_x \cdot npy + 6\ PEt_3 \xrightarrow{\text{tol, } 111°C} Mo_6Cl_{(8-x)}S_x \cdot 6PEt_3 + n\ py \qquad (8)$$

Because x was determined in this case solely by chlorine analysis, the value of x here was subject to high imprecision. The higher value of x though might indicate that the product of equation (8) that was insoluble in toluene and was filtered away, contained products with less than four sulfur atoms per cluster. Such compounds would best be formulated as $[Mo_6Cl_{(8-x)}S_x]Cl_{(4-x)} \cdot (2+x)L$. They should be somewhat polar due to the terminal chloride ligands and it would not be too surprising that their solubility properties would be different from the non-polar $Mo_6Cl_{(8-x)}S_x \cdot 6L$ compounds. This might explain the change in average $Cl:Mo_6$ ratio when going from the pyridine derivative to the triethylphosphine derivative. Another explanation would be that the cluster product of equation (7) was not completely free of the NaCl co-product as discussed above. Unfortunately, there is no evidence to support either alternative. No analytical data are available for the toluene insoluble material, which was a minor fraction of the total product. More complete analyses of these materials would also have provided the necessary information to answer this question.

Separations

Previous approaches to separate cluster products from one another on the basis of solubility differences proved to be insufficient. It is not surprising that the clusters with mixed chloride sulfide ligands have very similar solubility properties. Thus, chromatography was employed as the most feasible separations method. Because these compounds were expected to be nearly identical in structure and molecular weight, normal partition chromatography was the selected method.

Many column materials were found which would partially separate the cluster solutions. For this reason, a sequence of columns was employed. The most complete separation was obtained by using Celex-N-1 as a sort of "pre-column" before further separation on basic alumina. The cluster products isolated by this procedure fit the formulas $Mo_6S_8 \cdot 6PEt_3$, $Mo_6S_{\sim 5}Cl_{\sim 3} \cdot 6PEt_3$, and $Mo_6S_4Cl_4 \cdot 6OPEt_3$. $Mo_6S_4Cl_4 \cdot 6OPEt_3$ and $Mo_6S_{\sim 5}Cl_{\sim 3} \cdot 6PEt_3$ were major fractions with $Mo_6S_4Cl_4 \cdot 6OPEt_3$ being the most abundant. One problem with this separation system was a low capacity found for the basic alumina. Column overloading occurred for large samples. This may be a complication which arose from the presence of a substantial amount of water on the column surface. However, when separations were attempted using dried basic alumina, very little material could be eluted whatsoever. The water was in fact necessary to have the proper column activity.

The $Mo_6S_8 \cdot 6PEt_3$ cluster was the first to elute from basic alumina. In fact, it was not adsorbed at all. Fractions which were subsequently eluted from basic alumina contained increasingly more chlorine. Interaction between aluminum and

chlorine seems to be the retention mechanism. This is not unreasonable when the strength of aluminum-chlorine bonds is considered.

Although the yields were low for all fractions, some observations were made regarding the distribution of products. The $Mo_6S_4Cl_4$ cluster product was always the most abundant product. Mo_6S_8 and the fraction containing $Mo_6S_{\sim5}Cl_{\sim3}$ were also significant fractions, though the relative amounts of these seemed to vary from batch to batch. Those materials that eluted near $Mo_6S_8{\cdot}6PEt_3$ were always very minor amounts and enough for characterization was never isolated. However, the green species may be some derivative of $Mo_3S_4^{4+}$ which has been observed and identified in other preparations [47].

The most surprising result of this synthetic procedure was that the Mo_6S_8 cluster was produced, even when the ratio of sulfide to cluster during the substitution reaction was lower than eight. The formation of the Mo_6S_8 cluster from the reaction stoichiometry used here (4 sulfides per cluster), suggests that the fully sulfided compound is thermodynamically quite stable. The facile formation of $Mo_6S_8{\cdot}6PEt_3$ by the reduction of $Mo_3S_4Cl_4(PEt_3)_4(MeOH)$ at room temperature adds proof to its thermodynamic stability [24]. The formation of the completely sulfided $Mo_6S_8{\cdot}6PEt_3$ cluster by the methods used in this research seems to be dependent on the presence of base in the reaction mixture. When the cluster was reacted with seven equivalents of sodium hydrosulfide in the absence of base, no $Mo_6S_8{\cdot}6PEt_3$ was found in the product mixture [62]. The base probably deprotonates the hydrosulfide and prevents side reactions where insoluble H_2S would be formed and the sulfide source is subsequently depleted [15]. An analogous

occurrence is observed in the tungsten system. When W_6Cl_{12} is reacted with NaSH and NaOBu, W_6S_8 is the resulting sulfided cluster product, with little dependence on reaction stoichiometry [63].

Infrared Spectra

Infrared spectroscopy was a very valuable tool in the characterization of the materials prepared in this research. Mid-infrared and far-infrared spectra were obtained separately as previously discussed. The information obtained from these two sets of data was generally used for two different purposes. Organic constituents of the products were identified on the basis of the information found primarily in the mid-IR region while the far-IR spectra were used as an aid for determining if the cluster had remained intact throughout reaction. Tables II through IV contain the infrared absorption peaks found for all the products discussed in this section.

Mid-infrared spectra

Peaks found in the spectrum of the pyridine derivative were as expected. Confirmation for the presence of pyridine was given by the presence of fairly strong bands in the mid-infrared region near 1601 and 1443 cm^{-1} [64]. When compared to the spectra of previously characterized pyridine derivatives [15,16], one finds the same characteristic peaks near 1599, 1443, 1217, 1151, 1067, 1040, 1009, 754, and 692 cm^{-1}. Nothing out of the ordinary was observed.

The spectra of the triethylphosphine derivatives must be examined more closely. The fractions isolated from the chromatography gave spectra slightly

Table II. Absorption frequencies (cm^{-1}), found in the mid-infrared spectra of sulfided cluster products

A[a]	B[b]	C[c]	D[d]	E[e]	F[f]
1599(m)[g]					
1443(s)					
1416(m)	1416(m)	1416(mw)	1416(w)	1416(w)	1412(w)
		1261(m)	1261(mw)		1261(m)
	1252(m)		1250(w)	1254(mw,b)	
1217(m)					
1151(w)				1170(sh)	
				1105-1115(mw,b)	
		1097(mw,b)	1096(w,b)		1099(mw,b)
1067(mw)					
1040(m)	1036(s)	1032(ms)	1036(m)	1036(ms)	1034(m)
1009(w)	1001(w)				
	990(vw)		995(w)		
		802(m,b)	802(w)		802(w)
754(m)	764(s)	760(m)	764(ms,dbl)	766(ms)	766(mw)
	731(w)		730(vw,sh)	731(w)	
692(m)	690(w)		692(vw)		
667(w)			673(mw)		

[a]The cluster product of equation (7), $Mo_6Cl_{(8-x)}S_x \cdot npy$.
[b]The soluble cluster product of equation (8), $Mo_6Cl_{(8-x)}S_x \cdot 6PEt_3$.
[c]The first fraction collected from basic alumina, $Mo_6S_8 \cdot 6PEt_3$.
[d]PEt_3 derivative eluted from basic alumina column with CH_3CN.
[e]PEt_3 derivative eluted from basic alumina column with EtOH.
[f]PEt_3 derivative eluted from Celex-N-1 with acetonitrile.
[g]Relative intensities are given in parentheses: s=strong, m=medium, w=weak, sh=shoulder, b=broad, v=very, dbl=doublet.

different from the parent mixture. Samples obtained under the same conditions however gave the same spectra, supporting the reproducibility of the chromatographic procedure.

All spectra of the triethylphosphine-ligated materials contained the characteristic peaks of coordinated triethylphosphine: 1254, 1036, 764-770, and 730-731 cm^{-1} [65]. The relative intensities of these peaks were in agreement with those cited in the literature, while some of the peaks described in the literature as having weak intensities (1005, 980 and a group at 710, 680, and 641 cm^{-1}), were absent from these spectra or showed up only as weak shoulders. Also absent were the strong peaks characteristic of coordinated pyridine at 1443 and 631 cm^{-1}. This demonstrated that the ligand replacement was complete.

The spectra of those samples eluted with acetonitrile from basic alumina contained additional peaks at 1096, 673 and 536 cm^{-1}. The first was weak in intensity while the latter two were medium and strong respectively and are accounted for by the presence of triethylphosphine sulfide [66]. Strong bands at 670 and 535 cm^{-1} were reported in the literature for this compound. The band at 535 cm^{-1} is assigned to the P=S stretch [67,68]. Other strong peaks which correspond to vibrations of the ethyl groups were also reported. These occur at very nearly the same frequencies as the coordinated triethylphosphine.

In the ethanol eluted products, new IR peaks appeared at 1105 to 1115, 1069, and 448 cm^{-1} which were not seen in the spectrum of the mixture prior to chromatography. The parent mixture had never been exposed to air or moisture prior to the separations. However, the separations were done using dry nitrogen

purge whenever possible, but without pre-drying the eluents. It is therefore reasonable to presume these new peaks were from oxidation, hydrolysis, or ethanolysis products. It is not certain at this time however, exactly what these by-products were. One possibility is triethylphosphine oxide. The P=O stretching frequency of triethylphosphine oxide is reported to be at 1166 cm^{-1} [68]. The bands associated with the P=O stretch of triphenylphosphine oxide and trimethylphosphine oxide were found to shift to lower frequencies by approximately 40 to 70 cm^{-1} when coordinated [69]. The peak observed in the $Mo_6S_4Cl_4$ cluster compound at 1105 to 1115 may correspond to this vibration.

This is further supported by the absence of such a band in the spectrum of the product from the reaction of "$Mo_6S_4Cl_4 \cdot 6OPEt_3$" with triethylphosphine shown in the reaction below.

$$Mo_6S_4Cl_4 \cdot 6OPEt_3 + 6\ PEt_3 \longrightarrow Mo_6S_4Cl_4 \cdot 6PEt_3 + 6\ OPEt_3 \qquad (9)$$

This result suggested that the $OPEt_3$ was replaced by PEt_3. The spectrum of the ether soluble product suggests that it was indeed triethylphosphine oxide which was liberated in the reaction. (See Table III.)

The spectrum of the sample eluted from Celex-N-1 with acetonitrile was typical of a cluster compound with coordinated triethylphosphine. However, many of the peaks were not as intense as expected.

Table III. Absorption frequencies (cm^{-1}), found in the infrared spectra of the products and reactants of reaction (9)

$Mo_6S_4Cl_4 \cdot 6OPEt_3$	$Mo_6S_4Cl_4 \cdot 6PEt_3$	$OPEt_3$	$M \leftarrow PEt_3$[a]	$OPEt_3$[b]
Mid-IR:				
1558(w)[c]	1556(w)			1460(m)
1414(m)	1416(m)	1414(m)		1420(m)
1259(ms)[d]	1259(m,b)	1261(m,b)	1255(w)	1270(m)
	1167(w)	1161(ms,b)		1160(vs)
1105(s,b)				
	1099(m,b)			1050(m)
1036(s)	1036(s)	1042(w)	1033(s)	1030(w)
		~1020(w)		
~1000(sh)	~1000(vw)	1003(w)	1005(w)	
	980(vw)		980(vw)	960(w)
	951(mw)			
770(vs)	762(vs)	776(s)	765(s)	780(vs)
	733(w)		733(s)	725(w)
716(w)	716(m)		710(m)	700(w)
		696(m)	680(w)	
			641(m)	
Far IR:				
621(m)	623(ms)	616(vw,b)		
		479(m)		480(w)
446(w)	450(w)	449(vs)		448(s)
405(vs,b)	405(s)		413(m)	
	390(w)	390(sh)		
	365(w)	375(ms)	365(m)	
	344(w)	352(ms)		
	335(w)		335(m)	
	290(m)	292(m)		

[a]Literature values for coordinated triethylphosphine [65,70].

[b]Literature values for triethylphosphine oxide [68].

[c]Relative intensities are given in parentheses: s=strong, m=medium, w=weak, sh=shoulder, b=broad, v=very.

[d]The band near 1260 may be due to the presence of silicone grease in the samples.

Far-infrared spectra

Peaks assigned to cluster vibrations were found in all spectra. Therefore it can be said that the cluster remained intact throughout the reactions and separations. Specifically, the peaks at 620, 405-407, 390-391, 346-349, and 295-300 cm^{-1} were found in all the spectra, whether they were of pyridine or triethylphosphine derivatives.

The far-infrared spectrum of $[Mo_6Cl_8]Cl_4$ has two bands above 200 cm^{-1} [71]. These are located at 248 cm^{-1} and 329 cm^{-1} and have been attributed to stretching vibrations of Mo-Cl^a and the Mo-Cl^i-Mo bridges respectively [72]. The band at *ca.* 250 cm^{-1} was absent in all the spectra reported here, supporting the absence of any terminal chlorides in these products. Insertion of a single sulfur into one of the bridging positions resulted in the presence of a new band at 421 cm^{-1} in the infrared spectrum [13]. This band was assigned by Michel as a vibration of Mo-S character.

In a very general sense, these compounds showed two sets of bands associated with vibrations of the cluster. Bands at 346 and 300 were not present in $Mo_6S_8 \cdot 6PEt_3$ and are therefore assumed to arise predominantly from Mo-Cl contributions. The bands assigned as primarily Mo-S in nature were found at 391 and 410 cm^{-1}. In previous studies, the relative intensities of the bands associated with Mo-Cl and Mo-S vibrations were found to shift as more sulfur was substituted into the cluster [15,16]. Unfortunately, this phenomenon was not observed here due to the overlap of the δ(CCP) of the triethylphosphine ligand and the Mo-S band, *vide infra*. The absorption in this region predominated the far-IR region of the spectra. It also seems likely that in this region the bands would mix extensively and the result

would be vibrations resulting from the overall cluster, $[Mo_6Cl_{(8-x)}S_x]L_6$, and not necessarily from Mo-S or Mo-Cl [73].

Coordinated pyridine gives rise to strong characteristic bands in its far-infrared spectrum making it easy to identify [64]. The bands associated with in-plane and out-of-plane ring deformations are found at around 630 cm^{-1} and 430 cm^{-1}, respectively [74]. In the pyridine derivative, relatively strong bands at 631 cm^{-1} and 430 cm^{-1} further confirmed the presence of coordinated pyridine.

The bands at 334 cm^{-1} and 365 cm^{-1} seen only in the triethylphosphine derivatives were due to δ(CCP) bending modes of the triethylphosphine ligand [70]. An additional δ(CCP) mode is reported to occur at *ca.* 410 cm^{1-}. Since strong bands were observed at 405-407 cm^{1-} in all spectra, including the pyridine derivative, it is likely that this band overlaps another which arises from Mo-S vibrations. The metal-phosphorus stretching vibration is expected to occur below 250 cm^{-1}.

Table IV. Absorption frequencies (cm^{-1}), found in the far-infrared spectra of some sulfided molybdenum cluster compounds

A[a]	B[b]	C[c]	D[d]	E[e]	F[f]
	650(w)[g]				
631(s)					
620(m,vb)	621(s)	624(m)	622(m,b)	622(s,b)	617(m,b)
612(m,br)					
	600(w,vb)				
		559(w,b)	536(s)		
480(w,vb)	465(vw)	478(w,b)	480(w,b)		480(w,vb)
				448(w,b)	
430(m)					
405(s,b)	405(s,b)	404(ms)	406(s)	407(s,b)	405(s)
391(w,sh)	391(sh)	391(s)	390(sh)	390(sh)	390(w,sh)
	365(w)	365(w)	365(sh)	365(w)	
349(w,b)	346(w)		346(vw)	346(w)	
	334(w)	334(w)	334(vw)	334(w)	
295(m,b)			300(vw)	300(w)	
266(w,b)					

[a]Cluster product of equation (7), $Mo_6Cl_{(8-x)}S_x \cdot npy$.
[b]Soluble product of equation (8), $Mo_6Cl_{(8-x)}S_x \cdot 6PEt_3$, prior to chromatography.
[c]First fraction collected from basic alumina column, $Mo_6S_8 \cdot 6PEt_3$.
[d]PEt_3 derivative eluted from basic alumina column with CH_3CN.
[e]PEt_3 derivative eluted from basic alumina column with EtOH.
[f]PEt_3 derivative eluted from Celex-N-1 with acetonitrile.
[g]Relative intensities are given in parentheses: s=strong, m=medium, w=weak, sh=shoulder, b=broad, v=very.

^{31}P Nuclear Magnetic Resonance Spectra

The use of triethylphosphine as the terminal ligand was to aid in solubility of the product clusters, but also served as a means of studying the symmetry of the clusters by ^{31}P nmr. One can assume each phosphorus atom to have the same symmetry as the molybdenum atom it is coordinated to. Consequently, the number of symmetry independent molybdenum atoms should be the same as the number of independent phosphorus atoms. Resonances were observed downfield from the rest of the resonances in the spectra near 45 and 55 ppm. These were due to the presence of $O{=}PEt_3$ and $S{=}PEt_3$ respectively [75]. From the spectrum of the parent mixture shown in Figure 6, the presence of free triethylphosphine can be deduced from the band at -19 ppm from phosphoric acid [75]. Most likely, this uncoordinated ligand was the source of the oxidized products, triethylphosphine oxide and triethylphosphine sulfide. The triethylphosphine sulfide was probably formed in the reaction of the $Mo_6Cl_{(8-x)}S_x \cdot npy$ with triethylphosphine. The sulfide source would have been any SH^- or S^{2-} which incorporated into the terminal coordination sites of the cluster in the early steps of the sulfide substitution. It was not unreasonable for the triethylphosphine oxide product to be seen since the materials were not strictly kept from air during the chromatography.

The bands due to triethylphosphine ligands of cluster products are most likely those found in the region of 5 to 25 ppm. When coordinated, the resonance for triethylphosphine is shifted downfield by 40 ppm to as much as 70 ppm [76]. The strong resonance at 19 ppm was that of $Mo_6S_8 \cdot 6PEt_3$ [23].

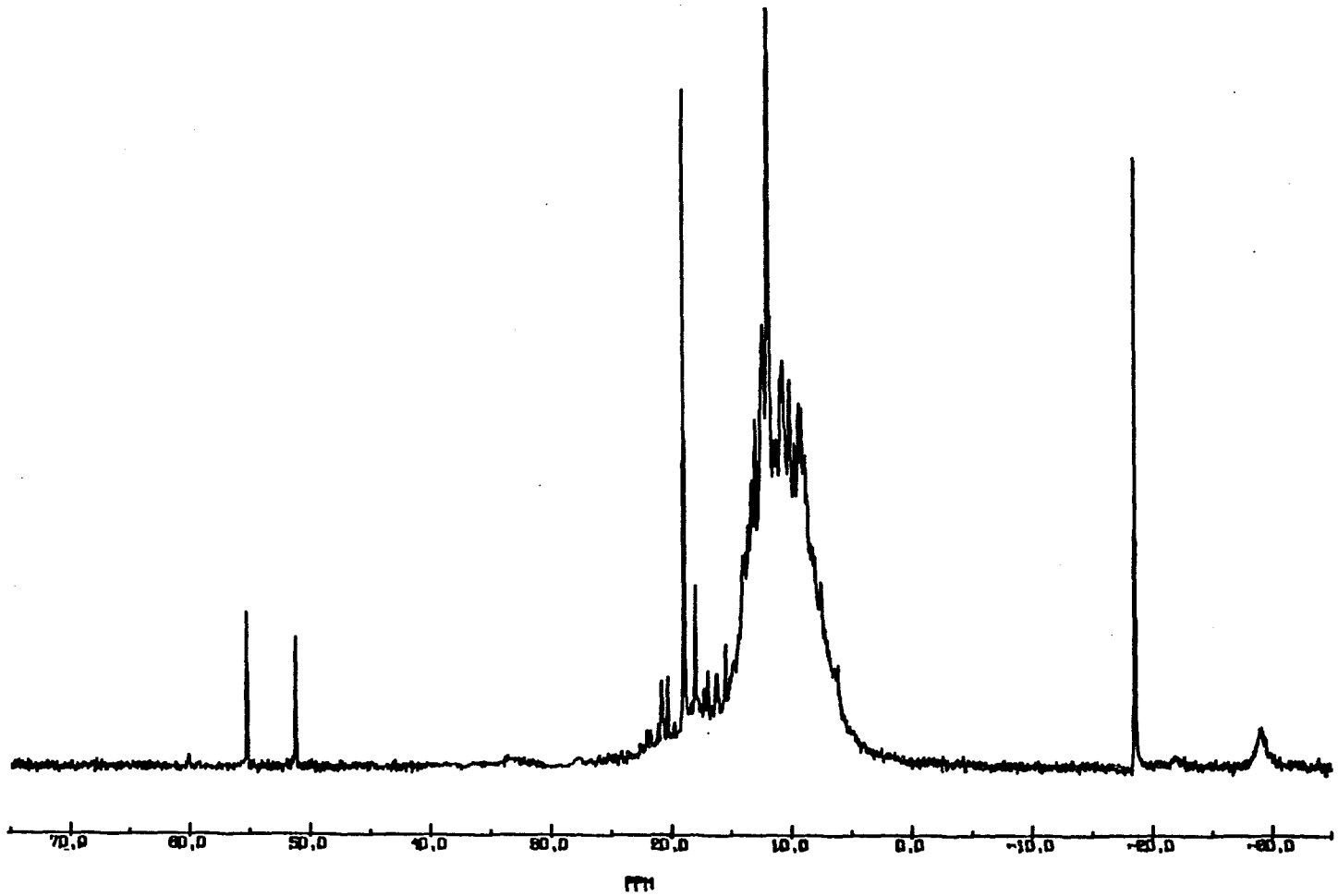


Figure 6. ^{31}Phosphorus nuclear magnetic resonance spectrum of $Mo_6Cl_{(8-x)}S_x \cdot 6PEt_3$ before chromatography

In the purified cluster products, these multiplets are only slightly simplified. In the ethanol eluted product (Figure 7), both $S{=}PEt_3$ and $O{=}PEt_3$ are present. Additionally, the cluster resonances occur in the region of 5 to 15 ppm, a smaller range than in the parent mixture, but these are still unresolved. The general shape of the "band" is such that it does appear to be caused by a large number of resonances and not just a single, broad band. Also, the band at 51 ppm which arises from $OPEt_3$ has much stronger relative intensity. A new weak broad band at 75 ppm may be due to coordinated $OPEt_3$. These results seem to point to the cluster being primarily coordinated by PEt_3 with $OPEt_3$ being an impurity.

The shape of the spectrum is not an entirely unexpected result when one considers the number of isomers of the $Mo_6S_4Cl_4$ cluster that can exist. A total of six different isomers with symmetries T_d, C_2, C_s, D_{2d}, C_{4v}, and C_{3v} are possible. In addition to the symmetrically independent phosphorus atoms each isomer would have, weak phosphorus-phosphorus coupling is also expected. The phosphorus atoms are separated by three bonds. With all this in mind one can see how a very complicated spectrum would arise in the absence of isomeric purity.

Electronic Structures

Up to four sulfides can be substituted into the bridging ligand sites of the $[Mo_6Cl_8]^{4+}$ cluster before oxidation is expected. The clusters would fit the general formula, $[Mo_6S_xCl_{8-x}]^{(4-x)+}$ $(0 \leq x \leq 4)$, and will have 24 electrons per cluster. Further substitution beyond four sulfides then would result in neutral, oxidized clusters with 20 to 23 electrons per cluster, $[Mo_6S_xCl_{8-x}]$, where $4 < x \leq 8$.

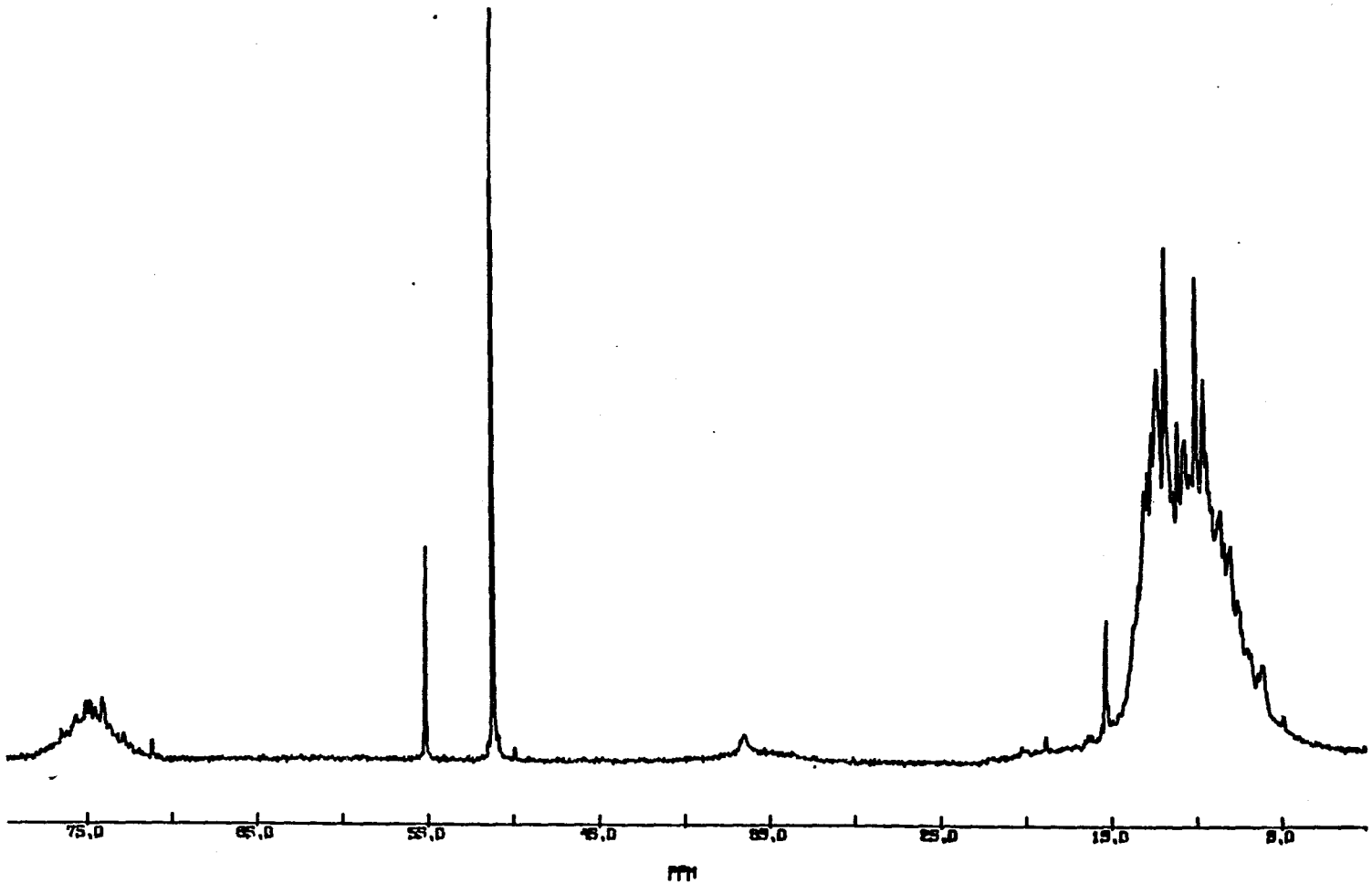


Figure 7. ^{31}Phosphorus nuclear magnetic resonance spectrum of "$Mo_6S_4Cl_4 \cdot 6OPEt_3$"

The three major fractions isolated by chromatography contain clusters that best fit the formulas $[Mo_6S_4Cl_4]$, $[Mo_6S_{\sim5}Cl_{\sim3}]$, and $[Mo_6S_8]$. The first and last are presumed to contain single stoichiometry clusters while the $[Mo_6S_{\sim5}Cl_{\sim3}]$ product is most likely a mixture of $[Mo_6S_5Cl_3]$ and $[Mo_6S_6Cl_2]$, and possibly even $[Mo_6S_7Cl]$. The $[Mo_6S_4Cl_4]$ cluster is expected to be a 24 electron cluster and should be diamagnetic. The $[Mo_6S_8]$ cluster is a 20 electron cluster and should also be diamagnetic. The final product must contain some $[Mo_6S_5Cl_3]$ which is most surely a paramagnetic 23 electron species. The UV/visible spectra and electron paramagnetic resonance spectra were used to confirm this.

UV/visible spectra

The electronic structure of the $[Mo_6X_8]^{4+}$ clusters has an e_g level as the HOMO level when 24 electrons per cluster are present. This level is filled for 24 electron species. The only possible electronic transitions are high in energy near the ultraviolet region, thus accounting for the yellow color of such clusters. Oxidation of the cluster leads to removal of electrons from the e_g level and allows for transition of electrons from the lower t_{2u} level up to the vacancies in the e_g level in the visible region of the spectrum. Thus, unoxidized species would not exhibit such a transition while oxidized species should. Such is the case observed for these compounds.

The spectra of the three major products are shown in Figure 8. As can easily be seen, the band at 591 is seen only in the spectrum of $Mo_6S_8{\cdot}6PEt_3$ and as a weak shoulder in the spectrum of $Mo_6S_5Cl_3{\cdot}6PEt_3$. It most likely arises from the transition from the highest t_{2u} level to the e_g level. It is absent in the spectrum of

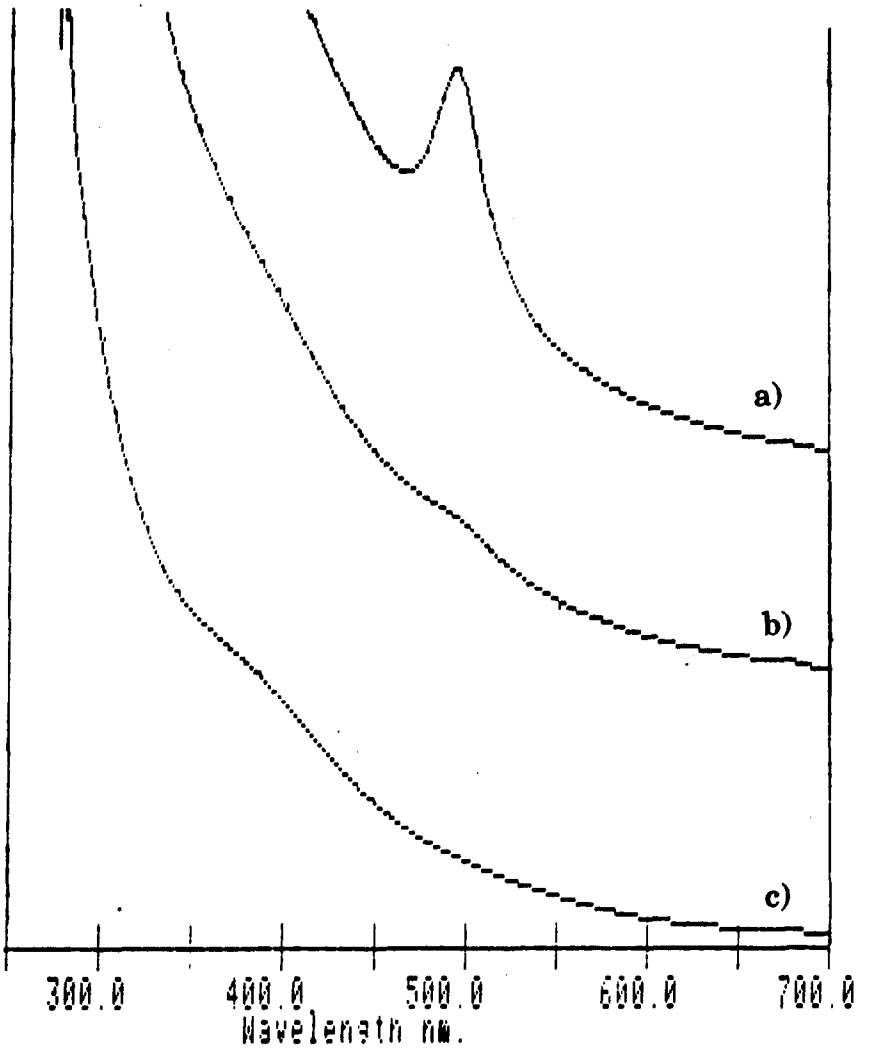


Figure 8. The electronic spectra of $Mo_6S_8 \cdot 6PEt_3$ (a), $Mo_6S_5Cl_3 \cdot 6PEt_3$ (b), and $Mo_6S_4Cl_4 \cdot 6OPEt_3$ (c)

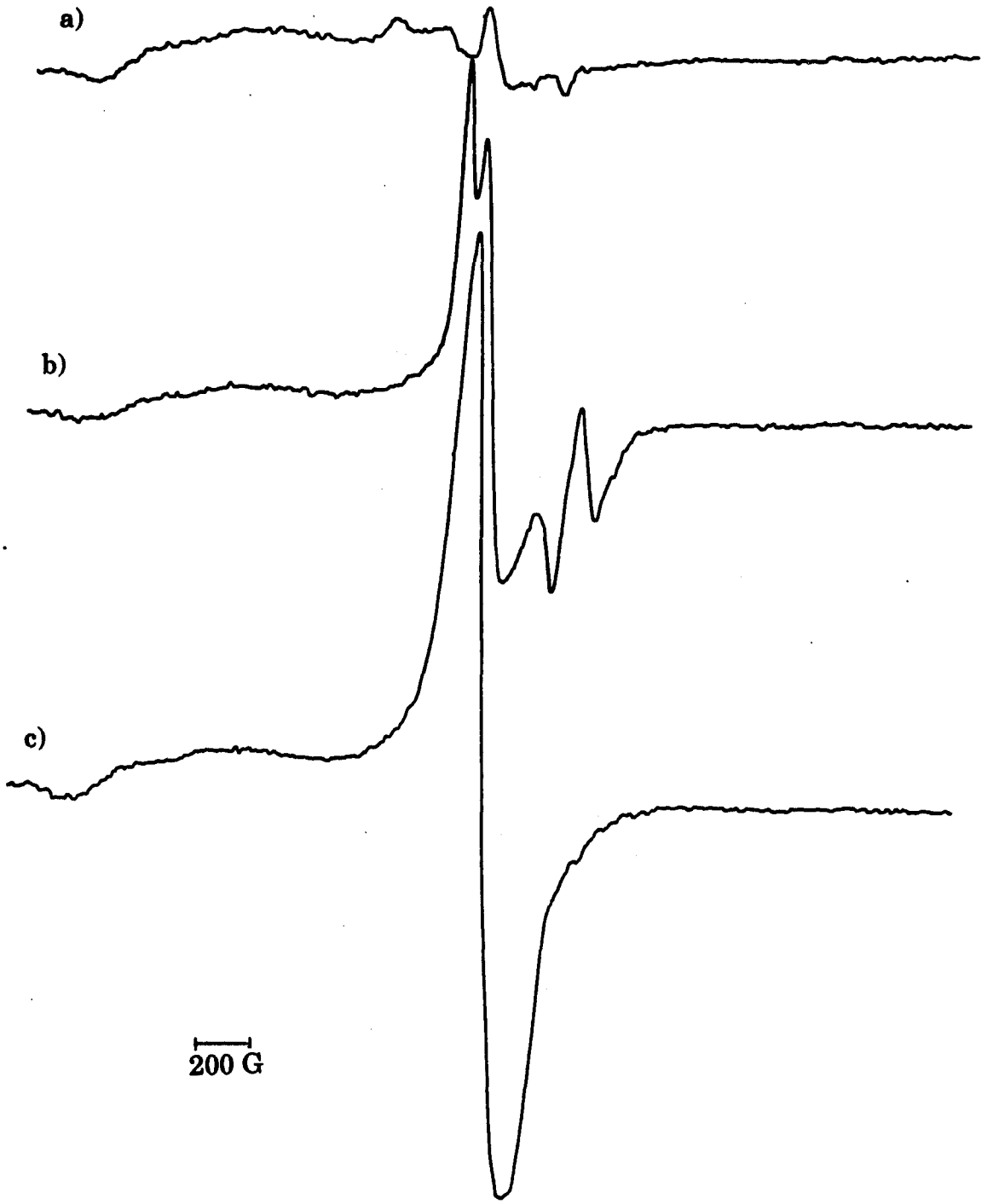
$Mo_6S_4Cl_4 \cdot 6PEt_3$. This indicates that indeed, the $Mo_6S_4Cl_4 \cdot 6L$ product contains no oxidized cluster. Unfortunately, the absorption is not resolved enough in the case of the $Mo_6S_5Cl_3$ cluster product to assign a precise wavelength and thus, make a comparison between the transitions of the two compounds. The probability that the $Mo_6S_{\sim 5}Cl_{\sim 3}$ product is a mixture of at least two different compositions ($Mo_6S_5Cl_3$ and $Mo_6S_6Cl_2$), may add to the poor resolution.

EPR spectra

The epr spectra of the products are shown in Figure 9. The signal from the $Mo_6S_8 \cdot 6PEt_3$ product is very weak, in accord with the expected diamagnetism of the species. An unexpected result is the strong signal from the $Mo_6S_4Cl_4$ sample. Because of the results reported above from the UV/visible spectrum of this material, it is presumed to arise from the presence of a paramagnetic impurity, and not an oxidized cluster species. Its shape and temperature dependence are significantly different from the spectrum of the $[Mo_6S_{\sim 5}Cl_{\sim 3}]$ product. At room temperature, no signal is observed at all for the $[Mo_6S_4Cl_4]$ product while the $[Mo_6S_{\sim 5}Cl_{\sim 3}]$ product does exhibit a spectrum.

The signal of the $Mo_6S_5Cl_3$ cluster product is worth examining more closely. It is not entirely straight forward. It appears that it may have more than one paramagnetic species. The first part of the spectrum looks like it arises from an unsymmetric species. The later peaks however are difficult to explain. Because the spectrum could only be scanned, that is, data could not be acquired, curve integration and model fitting could not be done. Also, in the absence of other spectra which may

Figure 9. The low temperature (113 K), epr spectra of $Mo_6S_8 \cdot 6PEt_3$ (a), $Mo_6S_5Cl_3 \cdot 6PEt_3$ (b), and $Mo_6S_4Cl_4 \cdot 6OPEt_3$ (c)


a)
b)
c)
200 G

show variations in relative intensities of the peaks and therefore provide information on which peaks arise from the same species, strict assignments of g-values is impossible.

CONCLUSIONS

The work described in Part 1 has confirmed that the sulfidation of Mo_6Cl_{12} occurs at moderate temperature (118°C), when Mo_6Cl_{12} is reacted with sodium hydrosulfide in the presence of base, sodium butoxide. The reaction of four equivalents of sodium hydrosulfide per cluster produces a mixture of sulfided clusters as products, including the completely sulfided Mo_6S_8 cluster species.

Separation of the mixture was accomplished on basic alumina columns, and best separations were obtained when a non-ionic cellulose column was used first. The retention mechanism was most likely the attraction between aluminum of the column and the chloride of the cluster. The $Mo_6S_8 \cdot 6PEt_3$ cluster was not adsorbed at all. The elemental analyses of the other products isolated fit the formulas $Mo_6S_{\sim 5}Cl_{\sim 3} \cdot 6PEt_3$ and $Mo_6S_4Cl_4 \cdot 6OPEt_3$ reasonably well. The $Mo_6S_{\sim 5}Cl_{\sim 3} \cdot 6PEt_3$ product is most likely a mixture of $Mo_6S_5Cl_3$ and $Mo_6S_6Cl_2$, and possibly Mo_6S_7Cl, cluster containing materials and exhibits a strong signal in the epr spectrum confirming the presence of an odd electron species such as $Mo_6S_5Cl_3$. Although the $Mo_6S_4Cl_4$ cluster containing product also showed a paramagnetic signal, the UV/visible spectrum did not indicate the presence of a reduced cluster by the absence of the absorption at around 590 nm. This band was observed in the spectra of the other products, confirming that they were reduced clusters.

Microcrystalline material was obtained by recrystallization of the major product, $Mo_6S_4Cl_4 \cdot 6OPEt_3$, from methylene chloride solution. Also, this material

was converted back to the $Mo_6S_4Cl_4 \cdot 6PEt_3$ species by reaction with excess triethylphosphine in refluxing toluene. Crystalline material of this compound was also obtainable but single crystals suitable for structure analysis were not.

The infrared spectra of the compounds confirmed the presence of coordinated triethylphosphine or triethylphosphine oxide. Also found in the spectra were absorption bands in the regions expected for cluster vibrations associated with primarily molybdenum-chlorine and molybdenum-sulfur vibrations.

Triethylphosphine oxide seemed to have been replaced by triethylphosphine when $Mo_6S_4Cl_4 \cdot 6OPEt_3$ was reacted with excess triethylphosphine in refluxing toluene. An x-ray powder pattern of the material revealed that it was to some extent crystalline but single crystals were not recovered.

PART 2. REACTIVITY OF $Mo_6S_8 \cdot 6PEt_3$: REMOVAL OF THE OUTER LIGANDS

INTRODUCTION

As a group of compounds, the Chevrel phases, $M_xMo_6S_8$ (M = Pb, Cu, and many other ternary metals), and also the metastable binary compound Mo_6S_8 possess many interesting properties [4]. Some of the compounds are superconducting at relatively high temperatures. The structure of these materials contains channels where the ternary metal atoms are found. These channels allow for high ionic conductivity of many ternary metal cations [7]. Furthermore, these materials exhibit catalytic activity for hydrodesulfurization [6]. Because of their interesting properties, this class of compounds has been extensively studied.

The ternary Chevrel phases are usually prepared by normal solid state methods at high temperatures. The binary, however, is unstable at temperatures above 468°C and is prepared only by first preparing a suitable ternary, which is subsequently oxidized with removal of the ternary metal ion [17]. For some time now, chemists have been looking into ways of preparing solid state materials, especially metastable compounds, from low temperature routes [18,19]. Many methods have been developed for the synthesis of metal oxides, nitrides, and also sulfides.

A low-temperature route to the binary Chevrel phase, Mo_6S_8, has become more realizable since the preparation of the molecular compound $Mo_6S_8{\cdot}6PEt_3$ [23,24]. This work reports attempts to prepare the Chevrel phase compound, Mo_6S_8, or a ternary phase, MMo_6S_8, by removal of the triethylphosphine ligands of the molecular $Mo_6S_8{\cdot}6PEt_3$ compound.

EXPERIMENTAL

Materials

Reagents

Mo_6Cl_{12}, or α-$MoCl_2$, was prepared by the high temperature conproportionation method described by Koknat *et al.* [58]. The compound was stored in a nitrogen atmosphere drybox (dewpoint -75°C). Sodium hydrosulfide was prepared by the method described by Brauer [59]. Hydrogen sulfide was bubbled through a solution of sodium ethoxide. The sodium hydrosulfide was recovered by precipitation from ether solution. Sodium butoxide was prepared by dissolution of sodium metal in dry butanol. The resulting solution was standardized by hydrolyzing an aliquot and diluting it to volume with distilled water. The hydroxide solution was then titrated against standard potassium hydrogen phthalate. The solution was stored under nitrogen and syringed as needed.

Calcium hydride was used to dry pyridine. Following a period of reflux over CaH_2, dry pyridine was obtained by fractional distillation under a slow flow of dry nitrogen, or by vacuum distillation onto 4Å molecular sieves. Triethylphosphine was used as obtained from Aldrich Chemicals and stored under dry nitrogen.

Molybdenum hexacarbonyl was used as obtained from Pressure Chemical Company. Dicobalt octacarbonyl was purchased from Strem Chemicals and kept refrigerated. It was sublimed prior to use. Propylene sulfide was obtained from Aldrich Chemicals and was stored under nitrogen in the refrigerator. Copper(I) chloride was obtained from Fisher Scientific and was dried at 140°C before use.

There was indication of an oxidized impurity due to the presence of a green color. A chlorine analysis however showed the impurity to be minor. (Calc. for CuCl: Cl, 35.81%. Found: Cl, 34.0%.) The cuprous chloride was used without purification and was stored in a desiccator.

Solvents

Butanol was dried with sodium metal and subsequently distilled onto outgassed 4Å molecular sieves. Methanol was purified by treatment with either sodium metal or sodium methoxide followed by vacuum distillation onto outgassed 3Å molecular sieves. Acetonitrile was refluxed over phosphorus pentoxide to remove water. Following this procedure, the acetonitrile was vacuum distilled onto outgassed 3Å molecular sieves. Toluene was dried by refluxing over calcium hydride. It then was distilled onto 4Å molecular sieves.

Analytical Procedures

Chlorine was determined by potentiometric titration of neutralized solutions with standard $AgNO_3$ solution using a Ag/AgCl electrode with a silver electrode as the reference. The endpoint was determined by the second derivative method. Microanalyses for molybdenum, sulfur, phosphorus, carbon, and hydrogen were obtained from Galbraith Laboratories [61].

Physical Measurements

Infrared Spectroscopy

Infrared spectra were obtained from an IR/90 Fourier Transform Infrared Spectrometer made by IBM Instruments, Inc. Samples were prepared as Nujol mulls. The mulls were pressed between cesium iodide plates to collect data. Reference spectra were obtained using an empty sample chamber. The sample chamber was constantly purged with nitrogen during the collection of data. Mid-infrared (4000-400 cm^{-1}), and far-infrared (600-200 cm^{-1}), spectra were recorded separately.

X-ray Powder Diffraction

An Enraf Nonius Delft FR552 Guinier camera was used to obtain x-ray powder patterns. A General Electric XRD-5 generator with a Philips normal focus tube and a Cu target was used to generate the x-rays. Air sensitive samples were ground thoroughly then mounted between strips of cellophane tape to protect them from air. Powdered NBS silicon was used as an internal standard.

Synthetic Methods

The procedure used to prepare $Mo_6S_8 \cdot 6PEt_3$ was developed by Laughlin and reported in reference 23. 6.0 g Mo_6Cl_{12} (6 mmol), and 2.7 g NaSH (48 mmol), were weighed in the drybox. 150 mL of dry *n*-butanol were syringed into the reaction flask under nitrogen flow. *Ca.* 11.5 mL of 2.03*M* NaOBu were syringed into the mixture

(24 mmol). Additionally, 5 mL of dry pyridine were syringed into the flask. The mixture was brought to reflux for 3 days.

After the initial reflux period, the reaction products were filtered. A colorless filtrate and dark brown solid resulted. A methanol extraction was begun and proceeded for 4 days. After this time, an orange filtrate and brown solid remained. The product was dried and further reacted with 0.68 g NaSH (12 mmol), in refluxing butanol for two days followed by another methanol extraction.

The resulting pyrophoric $Mo_6S_8 \cdot npy$ was further reacted with 16 mL (excess), of triethylphosphine in refluxing toluene for 24 hours to prepare the soluble $Mo_6S_8 \cdot 6PEt_3$ cluster. Filtering the products gave soluble $Mo_6S_8 \cdot 6PEt_3$ as the major product. It was stored in a nitrogen drybox before further reaction. The material was identified by its far-infrared spectrum. The insoluble fraction was pyrophoric and was probably an incompletely ligated species.

<u>Reaction of $Mo_6S_8 \cdot 6PEt_3$ with $Co_2(CO)_8$</u>

0.50 grams $Mo_6S_8 \cdot 6PEt_3$ (0.32 mmol), and 0.7 grams of freshly sublimed $Co_2(CO)_8$ (2.0 mmol), were dissolved in 40 mL of dry toluene. The mixture was stirred at room temperature for 2 days. Bubbling was observed for the first few minutes, indicating the evolution of CO. The reaction proceeded for 2 days before it was filtered and extracted with the reaction solvent for over a week. Yield: 0.2 g insoluble material, 0.7 g soluble material. Infrared spectra and microanalyses were obtained for the insoluble fraction. Found: Mo, 36.16%; S, 14.82%; P, 4.00%; C, 12.21%; H, 2.94%; S:Mo_6, 7.36; P:Mo_6, 2.06.

Reaction of $Mo_6S_8 \cdot 6PEt_3$ with molybdenum hexacarbonyl

1.0 gram of $Mo_6S_8 \cdot 6PEt_3$ (0.65 mmol), and 1.0 gram $Mo(CO)_6$ (3.8 mmol), were combined in the drybox. 30 mL of dry acetonitrile were syringed into the mixture. The mixture was brought to reflux with stirring.

Initially, no solubility was observed but as reflux temperature was achieved, the solution became darker. The reaction proceeded for 3 days before the mixture was filtered and extracted with the reaction solvent. Further extraction was done with toluene. Infrared spectra and an x-ray powder pattern were obtained for the insoluble fraction but no analyses were done on this material.

Reduction of the cluster with zinc in the presence of $Mo(CO)_6$

In an attempt to convert the isolated triethylphosphine cluster, $Mo_6S_8 \cdot 6PEt_3$, to the Chevrel phase, MMo_6S_8, where in this case M = Zn, the following reaction was attempted. 0.69 grams of $Mo_6S_8 \cdot 6PEt_3$ (0.45 mmol), *ca.* 0.03 g Zn metal (0.46 mmol), and 1.4 g $Mo(CO)_6$ (5.3 mmol), were combined in the drybox. 40 mL acetonitrile were vacuum distilled into the flask. The mixture was stirred and brought to reflux for 2 days. The resulting product mixture was filtered and the insoluble material was extracted with the reaction solvent. The x-ray powder diffraction pattern of the insoluble material showed only a single line which corresponded to the 100% relative intensity line of zinc metal.

Reaction of $Mo_6S_8 \cdot 6PEt_3$ with cuprous chloride

0.6 grams $Mo_6S_8 \cdot 6PEt_3$ (0.39 mmol) were combined with 0.23 grams CuCl (2.3 mmol) in drybox. 40 mL dry toluene were syringed into the flask and the mixture was brought to reflux for three days.

In contrast to the previous reactions discussed here, the filtrate resulting from this process was completely colorless. The filtrate was dried under vacuum. No material was recovered from this fraction. The insoluble material was extracted with dry toluene to remove any $[CuCl(PEt_3)]_4$ that may have been formed during reaction. Again, no material was isolated from the filtrate. An ethanol extraction was also done to remove any unreacted CuCl. A slight yellowing of the filtrate was observed, yet, very little material was recovered.

Infrared spectra were obtained for the insoluble material. An x-ray powder pattern was also obtained which showed no diffraction lines. Analysis: Calculated for $Mo_6S_8 \cdot 2PEt_3 \cdot 5CuCl$: Mo, 36.82%; S, 16.41%; C, 9.22%; H, 1.94%; Cl, 11.34%; P, 3.96%. Found: Mo, 36.73%; S, 17.47%; C, 8.78%; H, 1.85%; Cl, 10.80%.

Reaction of $Mo_6S_8 \cdot 6PEt_3$ with CuCl in acetonitrile

0.5 g $Mo_6S_8 \cdot 6PEt_3$ (0.3 mmol), and 0.22 g CuCl (2.2 mmol), were weighed in the drybox. 45 mL dry acetonitrile were syringed into the reaction flask under nitrogen flow. The mixture was brought to reflux for about 2 1/2 days. An extraction with the reaction solvent followed. The soluble fraction was dried *in vacuo*. Yield was 0.38 grams of insoluble material and 0.16 grams of soluble material. Analysis of the insoluble product: Found: Cl, 9.79%.

Reaction of $Mo_6S_8 \cdot 6PEt_3$ with propylene sulfide

1.00 g $Mo_6S_8 \cdot 6PEt_3$ (0.65 mmol) were dissolved in 30 mL dry toluene. 0.35 mL propylene sulfide (4.5 mmol) were syringed into the flask under nitrogen flow. The mixture was brought to reflux with stirring. Once reflux temperature was obtained, solid began to form along sides of the flask. Reflux was maintained for two days.

The resulting mixture was filtered. The major product was insoluble. An extraction with the reaction solvent was performed for 1 1/2 days. Yield was 0.79 grams of insoluble product. A mid-infrared spectrum was obtained for the insoluble fraction. Microanalyses were obtained. Calculated for $Mo_6S_8 \cdot 5SPEt_3$: Mo, 36.56%; S, 26.33%; C, 22.76%; H, 4.78%; P, 9.78%. Found: Mo, 34.23%; S, 24.69%; C, 18.99%; H, 3.60%; S:Mo_6 = 12.95.

The soluble material was dried as well. During this process, the material was slightly warmed and white needles sublimed above the heating mantle region. Infrared spectroscopy was used to determine that this colorless product was triethylphosphine sulfide.

The reaction of 0.5 grams of the insoluble material with a two-fold excess of triethylphosphine in refluxing toluene produced a soluble product. The filtered solution was dried at 0°C *in vacuo* to prevent loss of the fairly volatile triethylphosphine sulfide. The triethylphosphine sulfide was separated from the rest of the products by slight warming. The colorless triethylphosphine sulfide sublimed

to the cooler region of the vessel. Infrared spectroscopy confirmed the identity of this material. Yield of $SPEt_3$ = 0.18g.

RESULTS AND DISCUSSION

Syntheses

In each procedure described in this section, the goal was to remove all the triethylphosphine ligands from $Mo_6S_8 \cdot 6PEt_3$ to produce a Chevrel phase compound, either Mo_6S_8 or MMo_6S_8. In general, two approaches were taken. One was to react the molecular complex with a compound or complex which would act as a phosphine acceptor, with hope that phosphine transfer would occur. The second was to chemically alter the triethylphosphine ligand to give a non-coordinating or very weakly coordinating species.

Triethylphosphine is known to displace carbon monoxide in transition metal carbonyls. In this work, $Mo_6S_8 \cdot 6PEt_3$ was reacted with molybdenum hexacarbonyl and dicobalt octacarbonyl.

As written in equation (10), three equivalents of $Co_2(CO)_8$ are required to completely remove the PEt_3 ligands of the cluster.

$$Mo_6S_8 \cdot 6PEt_3 + 3\ Co_2(CO)_8 \rightarrow Mo_6S_8 + 3\ [Co(CO)_3(PEt_3)_2][Co(CO)_4] + 3\ CO \quad (10)$$

When this reaction was carried out at room temperature (the $Co_2(CO)_8$ species decomposes at 52°C), partial deligation of the molybdenum sulfide cluster occurred. Approximately 20% of the product was insoluble in toluene. This was taken as an indication that this product was no longer the completely ligated $Mo_6S_8 \cdot 6PEt_3$, but rather, was a species like $Mo_6S_8 \cdot nPEt_3$, where $n < 6$. The elemental analysis of this

product shows that phosphine ligand was lost during the reaction. The P:Mo ratio is 2.0 for the product. However, there is also evidence of other impurity because of the overall low percentages found. Dicobalt octacarbonyl or a derivative of this is probably present. Support for this is found in the mid-infrared spectrum of the material where there is evidence of the presence of carbonyl ligands.

When $Mo_6S_8 \cdot 6PEt_3$ was reacted with molybdenum hexacarbonyl according to equation (11), similar results were obtained.

$$Mo_6S_8 \cdot 6PEt_3 + 6\ Mo(CO)_6 \xrightarrow[82°C]{CH_3CN} Mo_6S_8 + 6\ Mo(CO)_{5-x}(PEt_3)(CH_3CN)_x \quad (11)$$

Elemental analysis was not done for this sample because of the likely presence of a molybdenum carbonyl complex.

Another approach to the transfer of phosphine ligands was to try to reduce the cluster simultaneously, that is, to prepare a ternary phase upon removal of the ligands.

$$Mo_6S_8 \cdot 6PEt_3 + Zn + 6\ Mo(CO)_6 \xrightarrow{L} ZnMo_6S_8 + 6\ Mo(CO)_3(PEt_3)L_2 \quad (12)$$

In this reaction, only a small fraction of the product was insoluble. Its powder pattern showed that metallic zinc remained unreacted. Thus, it is not likely that the cluster was reduced.

Copper(I) chloride is also known to form complexes with trialkylphosphines. The triethylphosphine derivative is a cubane-like species, $[CuCl(PEt_3)]_4$ [77]. Thus,

$Mo_6S_8{\cdot}6PEt_3$ was reacted with CuCl with hope that the triethylphosphine ligand would preferentially bind to the Cu rather than the Mo_6 cluster. The proposed reaction is written in equation (13).

$$Mo_6S_8{\cdot}6PEt_3 + 6\ CuCl \longrightarrow Mo_6S_8 + \frac{3}{2}\ [CuCl(PEt_3)]_4 \qquad (13)$$

The products of the above reaction performed in refluxing toluene were completely insoluble. The same reaction performed in acetonitrile however gave approximately 30% soluble material. The de-ligated material is not expected to be soluble. The copper complex is slightly soluble in toluene. Extraction of the products with toluene should have removed any unreacted cluster complex as well as any $[CuCl(PEt3)]_4$ formed in the reaction. Further extraction with ethanol was expected to remove any unreacted CuCl. The analysis of the dark brown insoluble product best fits a mixture of cluster complex and copper(I) complex. The presence of triethylphosphine is confirmed by the analysis, but no concrete evidence as to whether it is coordinated to the copper or to the cluster is available. A ratio of one cluster to 2 ligands to 5 CuCl entities is the best fit to the elemental analysis. This is curious since there is such a low ligand to cluster ratio yet still so high a copper(I) chloride to cluster ratio. Whether or not successful separation of the cluster from the copper(I) chloride species would also eliminate the ligand cannot be determined from the present data.

An alternate approach to "pulling off" the ligands of $Mo_6S_8{\cdot}6PEt_3$ was to chemically alter the ligand itself. In this work, formation of only very weakly

coordinating triethylphosphine sulfide was attempted. Reacting $Mo_6S_8 \cdot 6PEt_3$ with propylene sulfide was hoped to proceed as in equation (14).

$$Mo_6S_8 \cdot 6PEt_3 + 6\ CH_3\underset{S}{\underset{\diagdown}{CH}}\text{–}\underset{\diagup}{CH_2} \xrightarrow[111°C]{toluene} Mo_6S_8 + 6\ S{=}PEt_3 + 6\ CH_3CHCH_2 \quad (14)$$

The insoluble product's analysis however did not fit any reasonable cluster formula. The sulfur to molybdenum cluster ratio was far greater than 8, yet the expected sulfide product, triethylphosphine sulfide, was confirmed by infrared spectroscopy. One explanation is that the cluster was oxidized to MoS_2. This fits the sulfur to molybdenum ratio but is not indicated by the rest of the analysis or the infrared spectra. Characteristic peaks for MoS_2 at 385 and 470 cm^{-1} were also absent in the far-infrared spectrum [78].

The more likely possibility is that this species is a cluster with coordinated triethylphosphine sulfide. The reverse reaction of this product material with triethylphosphine in refluxing toluene produced a soluble product from which triethylphosphine sulfide was isolated. Also, the analysis fits the formulation of $Mo_6S_8 \cdot 5SPEt_3$ quite well. The replacement reaction is written below.

$$Mo_6S_8 \cdot 5SPEt_3 + 6\ PEt_3 \rightarrow Mo_6S_8 \cdot 6PEt_3 + 5\ SPEt_3 \quad (15)$$

The yield of triethylphosphine sulfide corresponded to only about 3.5 moles of $SPEt_3$ liberated per mole of starting cluster. This is slightly low but that is expected since

not all of the triethylphosphine sulfide could be recovered. Also, it is possible that some of the triethylphosphine sulfide was lost during the sublimation procedure.

Only the insoluble products of all the reactions described above were examined because de-ligation of the $Mo_6S_8{\cdot}6PEt_3$ cluster should give an insoluble product. If one ligand was removed, an open coordination site would become available and a bridging sulfide of another cluster would be a likely candidate to fill that open site. Thus, a dimer may be formed, $[(Mo_6S_7S^{i-a}_{1/2})S^{a-i}_{1/2}L_5]_2$. Further loss of terminal ligands is expected to result in further condensation of the cluster units to give material that is polymeric. To support this, many examples of pyridine derivatives of the sulfide chloride clusters are known where four ligands were found per cluster unit (*i.e.*, $Mo_6Cl_{(8-x)}S_x{\cdot}4py$) [15,16]. These materials were always insoluble and the value of four ligands per cluster did not vary greatly. Such a species might be formulated $[(Mo_6S_6S^{i-a}_{2/2})S^{a-i}_{2/2}L_4]_n$.

Consequently, in the reactions attempted here, removal of only two ligands, and possibly as few as one ligand, per cluster would most likely result in an insoluble, polymeric or oligomeric species. It is probable that once such a species is formed and falls out of solution, no further reaction would take place. Thus, the removal of all six terminal ligands was probably hampered by the insolubility of intermediate species, $Mo_6S_8{\cdot}nPEt_3$, where $n < 6$.

Other explanations must also be considered. The strong coordinating ability of the triethylphosphine ligand to the cluster is such a possibility. One of the earlier advantages of using triethylphosphine in the study of these clusters was to prepare a fully ligated and soluble cluster species. In order to break any Mo-S linkages

between clusters which formed in the first step of the sulfidation reaction, a strongly coordinating ligand was required. It may in fact be that the same properties of triethylphosphine that make it ideal for the preparation of the molecular cluster species, make $Mo_6S_8 \cdot 6PEt_3$ an undesirable candidate as a precursor to Mo_6S_8.

A further complication is that the products are amorphous to x-rays. They are not however pyrophoric as seen in some other incompletely ligated cluster species. The lack of crystallinity is no doubt a result of the low reaction temperatures. If in fact a low temperature route can be found to a de-ligated species, it will probably not produce a crystalline material. What effect the non-crystallinity would have on the properties of such materials is uncertain.

Infrared Spectra

Table V lists the infrared peaks observed for $Mo_6S_8 \cdot 6PEt_3$ and the products of the reactions described above. All compounds gave similar spectra. The peaks reported in the literature for coordinated triethylphosphine are also given for reference.

Peaks associated with the vibrations of coordinated triethylphosphine were observed to some extent in all spectra [65,70]. The strongest peaks arising from triethylphosphine ligand are found at *ca.* 1034 cm^{-1} and 760 to 765 cm^{-1} in the mid-IR region. A strong peak at 409 cm^{-1} and weaker but distinctive peaks at 365 and 334 cm^{-1} are found in the far-IR spectrum. The weaker peaks were absent, while the strong peaks had a much reduced intensity in the spectrum of the product of the reaction with propylene sulfide. In the product of reaction with CuCl, equation (13),

Table V. Absorption frequencies (cm^{-1}), found in the infrared spectra of $Mo_6S_8 \cdot 6PEt_3$ and products of deligation reactions

A[a]	B[b]	C[c]	D[d]	E[e]	$Et_3P \rightarrow M$[f]
Mid-IR Region:					
		1915(m)[g]		2006(w,b)	
1416(mw)	1420(w)	1416(w)	~1410(vw)	1410(w)	
1261(m)	1259(mw)	1259(m)	1261(w,b)	1256(w)	1255(w)
	1171(w)				
			1105(w,b)		
1097(mw,b)	1099(w)	1096(w)			
1032(ms)	1036(m)	1036(ms)	1040(w,b)	1034(ms)	1033(s)
	~1030(sh)				1005(w)
				920(w)	980(vw)
				845(w,b)	
802(m,b)	800(w)	804(mw)			
			783(ms)		
760(m)	766(w)	764(m)		766(m)	765(s)
					733(s)
					710(m)
					680(w)
Far-IR Region:					
624(m)	624(w)	623(mw)	626(w)	621(m)	641(m)
559(w,b)				555(m)	
478(w,b)			~490(w,sh)		
			455(ms,b)		
				428(w)	
404(ms)	402(mw)	404(ms)	411(s,b)	404(s)	413(m)
391(s)		390(sh)			
365(w)			372(m,b)		365(m)
334(w)				340(w,sh)	330(m)

[a] $Mo_6S_8 \cdot 6PEt_3$.
[b] The insoluble product of equation (14) done in toluene.
[c] The insoluble product of equation (11) done in CH_3CN.
[d] The insoluble product of equation (13) done in toluene.
[e] The insoluble product of equation (10) done in toluene.
[f] Literature values for coordinated triethylphosphine [65,70].
[g] Relative intensities given in parentheses: s=strong, m=medium, w=weak, v=very, sh=shoulder, b=broad.

these peaks were also much weaker than expected. In fact, the characteristic peak at 760 to 766 was absent in this product's spectrum. The spectra of all other products contained all of the characteristic peaks of $Mo_6S_8 \cdot 6PEt_3$ and some additional peaks.

The products of the reactions with transition metal carbonyls showed vibrations in the carbonyl stretching region (1900 to 2000 cm^{-1}). These were probably mixtures of cluster products and carbonyl complex. In the product of the reaction with CuCl, the bands at 783 and 455 cm^{-1} arise from the presence of CuCl. Its presence is expected from the elemental analysis. It appears however that none of the reactions produced a cluster product that was completely without the triethylphosphine ligand.

The reaction with propylene sulfide gave a product whose IR spectrum gave typical vibrations for a triethylphosphine derivative. The peaks were very broad and weak however, even those expected to be quite strong. No evidence for triethylphosphine sulfide, either free or coordinated, was observed. However, the reaction of this material with triethylphosphine definitely liberated triethylphosphine sulfide. The peaks for this material and the reverse reaction products are given in Table VI. It is possible that the peaks for $Mo_6S_8 \cdot 6PEt_3$ are weak and broad because of partial decomposition. The far-infrared peaks for PEt_3 are much less distinct than expected. This material was warmed slightly to allow the $SPEt_3$ to sublime away and this warming may have caused decomposition.

Table VI. Absorption frequencies (cm^{-1}), found in the infrared spectra of the reactants and products of equation (15)

$Mo_6S_8 \cdot 5SPEt_3$[a]	$SPEt_3$[b]	$Mo_6S_8 \cdot 6PEt_3$[c]
Mid-IR Region:		
1420(vw)[d]	1416(w)	1410(w)
1261(w,b)	1269(mw)	1258(wm)
	1246(m)	
	1163(m)	
1105(w,b)		
	1097(vw)	
1040(w,b)	1045(ms)	1034(m)
	995(ms)	
783(ms)	770(s)	762(mw)
	690(mw)	
	673(m)	
Far-IR Region:		
626(w)		623(w)
	536(s)	
490(w,sh)		
455(ms,b)		
411(s,b)	408(m)	
		391(w,vb)
372(m,b)		

[a]Product of equation (13).
[b]Colorless product of equation (15) sublimed from the rest of the products.
[c]Brown soluble product of equation (15) left after sublimation.
[d]Relative intensities given in parentheses: s=strong, m=medium, w=weak, v=very, sh=shoulder, b=broad.

CONCLUSIONS

In the research described here, attempts were made to convert $Mo_6S_8 \cdot 6PEt_3$ to a Chevrel phase compound. Unfortunately, the attempts were not successful. There is some evidence that phosphine ligand removal did occur. Products were insoluble and absorptions in the infrared spectra where the vibrations of coordinated triethylphosphine are expected were weak. Elemental analyses however showed that at least some triethylphosphine remained in all products. In the reaction with propylene sulfide, it appears that the ligands of $Mo_6S_8 \cdot 6PEt_3$ were indeed sulfided to give $Mo_6S_8 \cdot 5SPEt_3$. It is clear that complete de-ligation did not occur in any of the cases described.

In addition, difficulties in separation of reaction products existed. The amorphous nature of the products points to probable difficulties in obtaining crystalline materials from low-temperature reactions, even if complete de-ligation is accomplished.

PART 3. PREPARATION OF THIOETHER DERIVATIVES OF $Mo_6S_8 \cdot 6L$ BY LIGAND EXCHANGE

INTRODUCTION

A great deal of research has focussed on compounds that contain hexanuclear molybdenum clusters. The clusters, as found in Mo_6Cl_{12} and MMo_6S_8, are generally formed at high temperatures through solid state reaction methods [3,58]; however, the molecular compound, $Mo_6S_8 \cdot 6PEt_3$, can also be prepared by the reductive dimerization of $Mo_3S_4Cl_4(PEt_3)_4(MeOH)$ at room temperature [24].

Much is known about the reactivity of the molecular halide cluster compounds. Substitution of the terminal ligands of the halide clusters occurs with relative ease. The μ_3-ligands of the clusters can be substituted with other halides, alkoxides, and chalcogenides as well [13,42,44-47].

Since the discovery and characterization of the molecular cluster with sulfide bridging ligands mentioned above [23,24], the reactivity of this compound has been studied very little. Substitution of the terminal ligands of the octa-μ_3-sulfidohexamolybdenum cluster was examined here. Amine and phosphine derivatives of the neutral clusters, $Mo_6Cl_{(8-x)}S_x \cdot 6L$, have previously been prepared [15,16]. The goal of this study was to prepare a molecular cluster with sulfur donor ligands in the terminal positions. Because of the similarities to the Chevrel phases, these new compounds might be seen as molecular fragments of such materials. Also, the effect, if any, of the terminal ligand on the bonding within the cluster might be seen.

EXPERIMENTAL

Materials

Primary Reagents

Mo_6Cl_{12}, or α-$MoCl_2$, was prepared by the high temperature conproportionation method described by Koknat *et al.* [58]. The compound was stored in a nitrogen atmosphere drybox (dewpoint -75°C). Sodium hydrosulfide was prepared by the method described by Brauer [59]. Hydrogen sulfide was bubbled through a solution of sodium ethoxide. The sodium hydrosulfide was recovered by precipitation from ether solution. Sodium butoxide was prepared by dissolution of sodium metal in dry butanol. The resulting solution was standardized by hydrolyzing an aliquot and diluting it to volume with distilled water. The hydroxide solution was then titrated against standard potassium hydrogen phthalate. The solution was stored under nitrogen and syringed as needed.

Calcium hydride was used to dry pyridine. Following a period of reflux over CaH_2, dry pyridine was obtained by fractional distillation under a slow flow of dry nitrogen, or by vacuum distillation onto 4Å molecular sieves. *n*-Propylamine from Kodak Chemicals was used as obtained and was stored and transferred under vacuum.

Thioether reagents were obtained from Aldrich Chemical Co. and were used without further purification. Ethyl sulfide and tetrahydrothiophene (THT), were stored under nitrogen. Thiophene was stored and transferred under vacuum.

Solvents

Butanol was dried with sodium metal and subsequently distilled onto outgassed 4Å molecular sieves. Methanol was purified by treatment with either sodium metal or sodium methoxide followed by vacuum distillation onto outgassed 3Å molecular sieves. Acetonitrile was refluxed over phosphorus pentoxide to remove water. Following this procedure, the acetonitrile was vacuum distilled onto outgassed 3Å molecular sieves. Toluene was dried by refluxing over calcium hydride then distilled onto 4Å molecular sieves.

Physical Measurements

Infrared spectroscopy

Infrared spectra were obtained from an IR/90 Fourier Transform Infrared Spectrometer made by IBM Instruments, Inc. Samples were prepared as Nujol mulls. The mulls were pressed between cesium iodide plates to collect data. Reference spectra were obtained using blank cesium iodide plates or air. The sample chamber was constantly purged with nitrogen during the collection of data. Mid-infrared (4000-400 cm^{-1}), and far-infrared (600-200 cm^{-1}), spectra were recorded separately.

X-ray powder diffraction

An Enraf Nonius Delft FR552 Guinier camera was used to obtain x-ray powder patterns. A General Electric XRD-5 generator with a Philips normal focus tube and a Cu target was used to generate the x-rays. Air sensitive samples were ground

thoroughly then mounted between strips of cellophane tape to protect them from air. Powdered NBS silicon was used as an internal standard.

Synthetic Methods

Preparation of $[Mo_6S_8]\cdot npy$

The procedure used to prepare the Mo_6S_8 cluster was developed by Laughlin and reported in reference 23. A modified version was used here. 6.0 g Mo_6Cl_{12} (6 mmol), and 2.7 g NaSH (48 mmol), were weighed in the drybox. 150 mL of dry *n*-butanol were syringed into the reaction flask under nitrogen flow. *Ca.* 11.5 mL of 2.03*M* NaOBu were syringed into the mixture (24 mmol). Additionally, 5 mL of dry pyridine were syringed into the flask. The mixture was brought to reflux for 3 days.

After the initial reflux period, the reaction products were filtered. A colorless filtrate and dark brown solid resulted. A methanol extraction was begun and proceeded for 4 days. After this time, an orange filtrate and brown solid remained. The product was dried and further reacted with 0.68 g NaSH (12 mmol), in refluxing butanol with added pyridine for two days followed by another methanol extraction.

Preparation of $Mo_6S_8\cdot 6Pr^nNH_2$

The pyridine derivative obtained from the above procedure was dried, then extracted with neat *n*-propylamine. The resulting solution was then stripped of solvent under a dynamic vacuum. The compound was identified by its infrared spectrum.

Reaction of Mo_6S_8·npy with thiophene

0.5 grams of Mo_6S_8·npy (*ca.* 0.4 mmol) were weighed in the drybox. Approximately 35 mL of thiophene were vacuum distilled into the reaction flask. The mixture was brought to reflux with stirring for 24 hours. Filtration of the products resulted in a colorless filtrate and dark brown solid. The insoluble fraction was extracted with toluene to recover any soluble product but none was obtained. Infrared spectra of the insoluble product were obtained.

Reaction of Mo_6S_8·npy with ethyl sulfide

0.5 grams of Mo_6S_8·npy (*ca.* 0.4 mmol) were weighed in the drybox. Approximately 35 mL of ethyl sulfide were syringed into the reaction flask under nitrogen flow. The mixture was brought to reflux with stirring for 24 hours. Filtration of the products resulted in a pale pink filtrate and dark brown solid. The insoluble fraction was extracted with ethyl sulfide. The filtrate was stripped under vacuum and toluene was used to further extract the insoluble material in the same vessel. An extraction with acetonitrile also failed to provide any soluble material. Infrared spectra of the insoluble and soluble material were obtained.

Reaction of Mo_6S_8·npy with tetrahydrothiophene

0.5 grams of Mo_6S_8·npy (*ca.* 0.4 mmol) were weighed in the drybox. Approximately 35 mL of tetrahydrothiophene (THT) were syringed into the reaction flask under nitrogen flow. The mixture was brought to reflux with stirring for 24 hours. Filtration of the products resulted in a pink filtrate and dark brown solid.

The insoluble fraction was extracted with toluene to recover further material but very little material extracted. Infrared spectra of the insoluble material were obtained. The filtrate was placed in the refrigerator to promote crystal growth. After several weeks, solid had come out of solution but no signs of crystallinity were seen.

Reaction of $Mo_6S_8 \cdot 6Pr^nNH_2$ with THT

0.25 grams of $Mo_6S_8 \cdot (6\text{-}x)PrNH_2$ were weighed in the drybox. *Ca.* 30 mL of THT were syringed into the reaction flask under nitrogen flow. The mixture was stirred and brought to reflux for 24 hours. Upon filtration, a dark purple solution and brown solid were obtained. Allowing the solution to sit at room temperature under a partial vacuum produced crystalline material. If allowed to sit for more than a few days, the solution turned to a brown color but any crystalline solid recovered from the solution was still purple when ground. Infrared and UV/visible spectra were obtained for the crystalline material. This material appears to be air stable for periods of at least a few months.

Crystallographic Data Collection and Treatment

Single crystals of $Mo_6S_8 \cdot 6THT$ were obtained from saturated THT solutions. Several cube-shaped crystals were examined. These purple crystals appeared to be well formed single crystals. Crystals were mounted in thin walled capillaries using silicone grease or to glass fibers using epoxy. All of the crystals showed signs of twinning to some extent in their peak profiles. A 0.08 mm x 0.08 mm x 0.08 mm crystal mounted in a capillary gave the best peak profiles and was chosen for data

collection. Data were collected at room temperature on a Rigaku AFC6R four-circle diffractometer with a rotating anode source from Molecular Structure Corporation.

Two sets of data were actually collected. A unique set was collected first. One octant of reflections with 2θ values from 0 to 50° was collected. A total of 4248 reflections were measured with 394 observed. The data set was worked up using the TEXSAN software package [79]. MITHRIL [80], a direct methods program, was used to determine the position of the unique Mo atom and the other atoms were determined from electron density maps. A partial structure was solved in the *I*a3 space group. However, when the R-factor got down to about 12 to 15%, the refinement began to diverge. Re-examining the data and output more critically revealed that the data were not properly averaged. Also, the R-factor of averaging seemed to indicate that the Laue symmetry as well as the space group were incorrectly determined. Because of the limited number of data, working in a lower symmetry to refine the structure was impossible. Thus, a new set of data was collected. It became clear after much more work that the TEXSAN software is incompatible with cubic systems.

With the second data set, a full hemisphere of reflections was scanned so that enough redundant data would be available for averaging. Standards chosen from a working set of 18 reflections were those with the best peak profiles. They were measured every 200 reflections and very little deviation in intensity was seen. In this set, a total of 24,317 reflections with $0° < 2\theta < 50°$ were collected. Of these reflections, approximately 10% were observed. Crystal data and collection

information are listed in Table VII. Scattering factors were taken from Cromer and Weber [81]. Hydrogen scattering factors were taken from Stewart *et al.* [82].

This data set was averaged using the CHESCAT software package. At first, the Laue symmetry $\bar{3}$ and the trigonal space group $R\bar{3}$ were used. An R of averaging of 4.7% was obtained. Rhombohedral axes were used so that the previous partial structure in the cubic system could be easily used as the model. The initial positions of the molybdenum atoms were determined by using the position from the previous structure and transforming it according to the differences in the orientation matrices of the two sets of data. Finally, the positions were transformed according to the four different possible orientations of the three-fold axis in the cubic system to find the one which corresponded to the unique axis of the trigonal system. The rest of the molybdenum positions and the sulfur positions were determined from electron density maps. The R-factor for this system went as low as 12 to 14% before the refinement diverged, clearly indicating the wrong choice of space group.

Further work was then done to determine the true symmetry of the lattice. Superposition methods and a symmetry location program were used. The symmetry location output suggested that the system might be monoclinic and a great deal of effort went into determining the possible space group. Averaging the data in the Laue symmetry 2/m gave an R of averaging of 2.9 to 3.1%, depending on the definition of the unique axis. However, a good model was never found for these systems.

Throughout the work to determine the symmetry and space group, it became clear that the R of averaging obtained from the TEXSAN software was erroneous and

Table VII. Crystallographic data for $Mo_6S_8 \cdot 6THT$

A. Crystal Data

formula	$Mo_6S_8(SC_4H_8)_6$
molecular weight	1361.2
crystal system	cubic
space group	*I*a3
systematic absences	hkl, h+k+l=2n+1; hk0, h(k)=2n+1 h0l, h(l)=2n+1; 0kl, k(l)=2n+1
cell dimensions	
a, Å	20.313 (5)
V, $Å^3$	8381.3
Z	8
d_{calcd}, g/cm^3	1.299
crystal morphology	
color	purple
crystal shape	cubic
crystal size, mm	0.08 x 0.08 x 0.08
μ (Mo Kα), cm^{-1}	23.941, (not applied)

Table VII (continued).

B. Data Collection Parameters	
instrument	Rigaku AFC6R
radiation	Mo Kα, graphite monochromated λ=0.7107Å
temperature, °C	20
no. of orientation reflections	18
scan method	2θ-ω
standard reflections	
number monitored	3
frequency measured	every 200 reflections
intensity variation	less than 2%
data collection range	$2.00 \leq 2\theta < 50°$
octants collected	h, ±k, ±l
no. of reflections measured	24,317
no. of reflections with $F_o > 3\sigma(F_o)$	2767

C. Structure Solution Information	
no. of averaged data	227, R=4.58%
refl/parameter	4.8
R^a	6.0%
$R_w{}^b$	4.6%

[a] $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$.

[b] $R_w=\Sigma w(|F_o|-|F_c|)^2/\Sigma w\,|F_o|^2$, $w=1/\sigma(F_o)^2$.

meaningless. Finally, the data were carefully examined by visual inspection. Several sets of reflections with permuted indices were compared. The observed intensities and extinctions most closely agreed with the *I*a3 space group. When the data set was averaged in the Laue symmetry m3 using the CHESCAT software, an R of averaging of 4.6% was obtained.

The space group *I*a3 and this newly averaged data set were used for the rest of the structure solution. Finding the unique Mo position was difficult. Because of an unidentified error the direct methods program (MULTAN80) [83] in this software package could not be used. The Mo positions of the previous partial solutions were also incorrect. Finally, MITHRIL was run through the TEXSAN software on the unaveraged or reduced data. A unique solution was obtained and the molybdenum position was correct. It was noted that the difference in the position determined with the second data set from the first was a shift of the origin by ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$). Further calculations were done using the CHESCAT programs [84]. With the unique Mo position in the refinement, an R-factor of 27.6% was achieved after 2 cycles. Sulfur and carbon atoms were located from subsequent electron density maps. With the addition of the sulfur atoms, an R-factor of 12.3% was achieved. The final positional parameters are given in Table VIII. Because of the limited data, the carbon atoms were refined isotropically.

Table VIII. Fractional atomic coordinates ($x10^4$), and isotropic temperature factors ($Å^2$, $x10^3$), for $Mo_6S_8 \cdot 6THT$[a]

Atom	x	y	z	U or U_{ave}
Mo	4588 (2)	5271 (2)	4226 (2)	39[b]
S(1)	5571 (5)	4920 (5)	3654 (5)	46[b]
S(2)	4160 (6)	4160 (6)	4160 (6)	49[b]
S(3)	4005 (7)	5640 (6)	3158 (6)	66[b]
C(1)	4582 (22)	6031 (25)	2653 (22)	79 (16)
C(2)	4464 (31)	6670 (30)	2543 (30)	117 (22)
C(3)	3974 (34)	6869 (27)	2870 (30)	124 (25)
C(4)	3584 (27)	6393 (30)	3293 (28)	117 (22)

[a]Estimated standard deviations are given in parentheses and apply to the preceding digit.

[b]For the atoms which were varied anisotropically, U_{ave} is given where U_{ave} is the average of U_{11}, U_{22}, and U_{33}.

DISCUSSION

Substitution Reactions

Substitution of the outer ligands of mixed sulfide chloride clusters was studied by Laughlin [15]. In that work it was found that soluble *n*-propylamine and trimethylphosphine derivatives were formed upon substitution of $Mo_6S_8 \cdot npy$. The triethylphosphine derivative was found to form under somewhat more forcing conditions [23]. These were all soluble clusters with no intercluster Mo-S-Mo linkages. In this study, solubility was used as an indicator for complete substitution and ligation of the cluster.

Replacement of pyridine and the disruption of intercluster Mo-S-Mo linkages by thioether ligands did not take place to any significant extent under the conditions used here. Reaction of $Mo_6S_8 \cdot npy$ with neat ethyl sulfide, thiophene, and tetrahydrothiophene (THT), at reflux temperatures provided very little soluble material to isolate. In the case of thiophene, it appears that no reaction took place. With ethyl sulfide, hardly enough sample was isolated to get an infrared spectrum. More product was isolated from the soluble fraction of the THT substitution, but this was still not the major product.

It was shown in previous work that the *n*-propylamine ligand could be partially stripped from the cluster under vacuum at room temperature [15]. For this reason, the formula is denoted here as $Mo_6S_8 \cdot (6\text{-}x)PrNH_2$, where x increases with the time under vacuum. Because the ligands were so easily removed, it seemed a

good idea to try replacing the ligands of this derivative. In this case, only THT was tried due to its greater success in replacing the pyridine.

In refluxing neat THT, the replacement seems to go fairly extensively. A very concentrated solution was achieved which gave crystalline material upon sitting for only one to two days. The solutions are not stable for more than a few days to a week. The solid however seems to be stable in air for at least several months.

Structure of $Mo_6S_8 \cdot 6THT$

A diagram of the $Mo_6S_8 \cdot 6THT$ cluster is shown in Figure 10. The clusters are centered on the corners, edges, face centers, and the body center of the unit cell. The unit cell with only the Mo_6 clusters is shown in Figure 11. The clusters are centered on sites of local $\bar{3}$ symmetry. Two of the eight bridging sulfur atoms lie on the 3-fold axis. The 3-fold symmetry of the cluster is demonstrated in Figure 12a. Figure 12b clearly shows the orientation of the ligands. Each THT ring bends over the cluster to leave the bridging sulfur atoms which are on the 3-fold axis exposed.

Tables IX and X give bond lengths and angles of the cluster. Information on the ligand bonds and angles can be found in the Appendix. The Mo-Mo bond lengths are all equivalent, within experimental error. Thus, the clusters have nearly perfect octahedral symmetry. All bond lengths within the cluster are nearly the same as the triethylphosphine derivative [24]. However, the Mo-Mo bond distance of the THT derivative is about 2.64Å, somewhat shorter than the bond length of 2.66Å found for $Mo_6S_8 \cdot 6PEt_3$. This difference may in fact be due only to the large standard deviations of the bond lengths found for $Mo_6S_8 \cdot 6THT$.

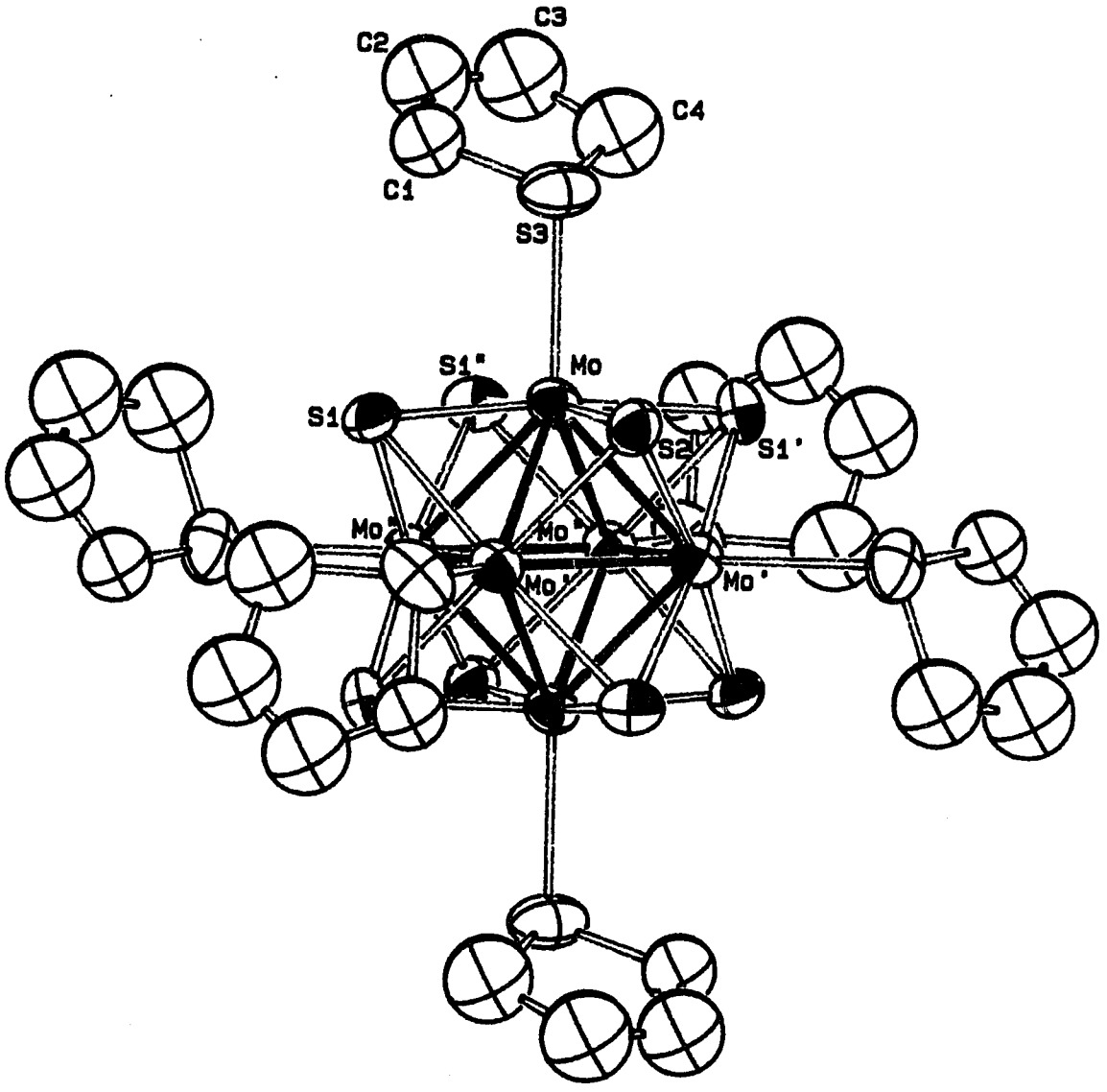


Figure 10. ORTEP diagram of $Mo_6S_8 \cdot 6THT$ with atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level

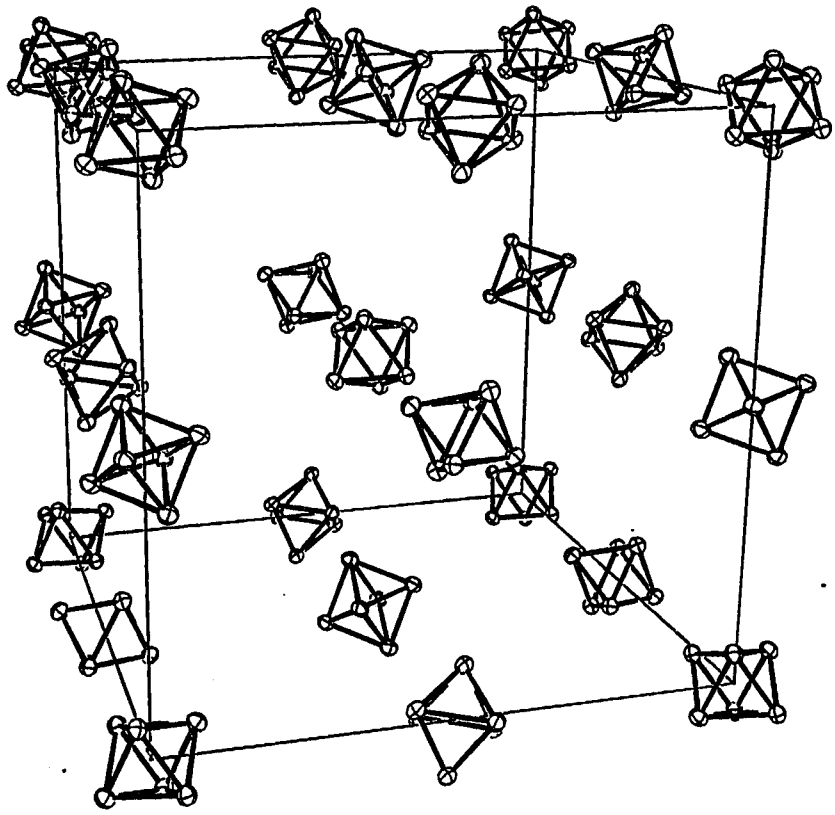
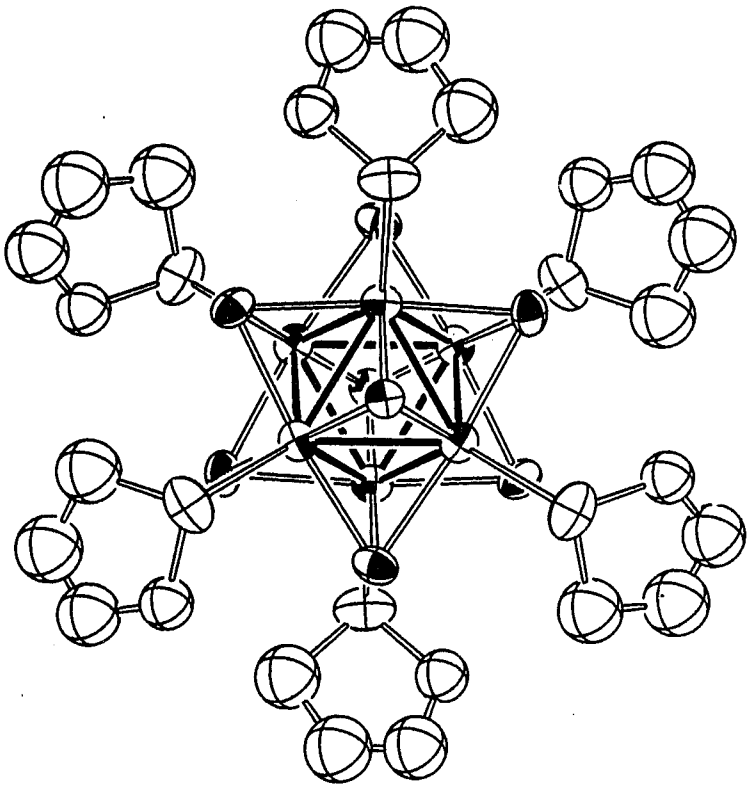


Figure 11. View of the unit cell of $Mo_6S_8 \cdot 6THT$ showing the Mo_6 clusters

a)



b)

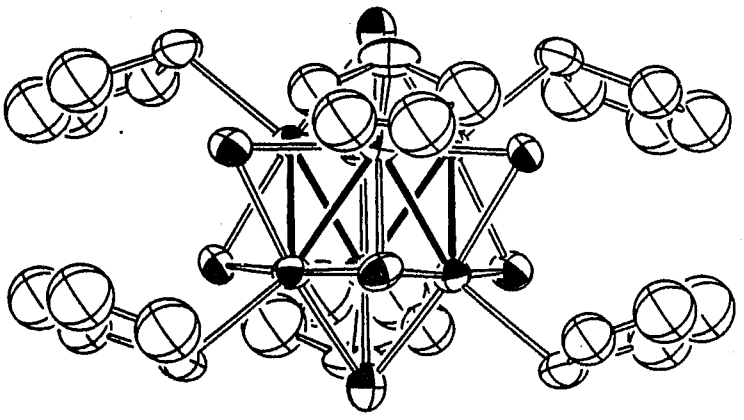


Figure 12. Additional views of $Mo_6S_8 \cdot 6THT$ looking down the 3-fold axis (a), and with the 3-fold axis oriented vertically along the page (b)

Table IX. Selected bond distances (Å), in $Mo_6S_8 \cdot 6THT$[a]

Mo-Mo'	2.639 (6)	Mo-S(2)	2.42 (2)
Mo-Mo"	2.633 (6)	Mo-S(3)	2.58 (1)
Mo-S(1)	2.42 (1)	S(3)-C(1)	1.75 (5)
Mo-S(1)'	2.44 (1)	S(3)-C(4)	1.77 (5)
Mo-S(1)"	2.44 (1)		

[a]Standard deviations are given in parentheses and refer to the preceding digit.

Table X. Selected bond angles (deg), in $Mo_6S_8 \cdot 6THT$[a]

Mo'-Mo-Mo'	60.0 (0)	S(3)-Mo-S(1)	93.4 (4)
Mo'-Mo-Mo"	59.9 (1)	S(3)-Mo-S(1)'	93.2 (4)
Mo"-Mo-Mo"	60.2 (2)	S(3)-Mo-S(1)"	94.0 (4)
Mo'-Mo-Mo"	90.0 (0)	S(3)-Mo-S(2)	93.4 (4)
S(1)-Mo-S(1)	90.4 (3)	Mo-S(1)-Mo'	65.8 (3)
S(1)-Mo-S(2)	89.7 (3)	Mo-S(1)-Mo"	65.7 (3)
S(1)'-Mo-S(1)"	89.9 (3)	Mo'-S(1)-Mo"	65.3 (3)
S(1)'-Mo-S(2)	89.2 (3)	Mo-S(2)-Mo'	66.1 (5)
S(1)-Mo-S(1)'	173.3 (4)	Mo-S(3)-C(1)	109. (2)
S(1)"-Mo-S(2)	172.6 (4)	Mo-S(3)-C(4)	110. (2)

[a]Standard deviations are given in parentheses and refer to the preceding digit.

Some difference in Mo-Mo bond length may be expected based on the nature of the donor ligand. The cluster orbitals that are oriented toward the terminal ligands are somewhat antibonding with respect to the Mo-Mo bonds of the cluster. Increased donation of electron density to these orbitals may have a Mo-Mo bond lengthening effect. Unfortunately, there is simply not enough information available at this time to make substantiated claims regarding the effect of coordinated ligand on Mo-Mo bond lengths.

Infrared Spectroscopy

The purpose of infrared spectroscopy was to determine whether or not and to what extent the substitution of the terminal ligands took place. The soluble products of the substitutions described above were examined. The observed peaks are listed in Table XI. The starting materials $Mo_6S_8 \cdot npy$ and $Mo_6S_8.(6\text{-}x)PrNH_2$ gave characteristic spectra. The spectrum of the pyridine derivative shows peaks at 1601 and 631 cm^{-1} confirming the presence of pyridine [64,74]. The peaks at 1566 and 860 in the spectrum of $Mo_6S_8.(6\text{-}x)PrNH_2$ confirm the presence of *n*-propylamine [85] and the absence of the strong bands for coordinated pyridine confirm the substitution is complete.

For the ethyl sulfide substitution, a very low yield was achieved. Because of this, only a very weak mull could be prepared and therefore only very weak peaks were observed. In this case, it is difficult to state with certainty that the substitution did in fact take place. The few peaks observed do suggest however that it has. Strong peaks for coordinated pyridine at 1601 and 1443 cm^{-1} are absent while new

peaks at 1097 and 802 cm^{-1} are seen. These arise from the presence of coordinated ethyl sulfide [86].

The spectrum of the product of the reaction of the propylamine adduct with THT confirms that this is indeed material with the ligands completely replaced by THT. Distinct peaks at 1306, 1269, 1254, 1130, 1070, 1035, 957, 879, and 808 cm^{-1} in the mid-IR region all correlate to peaks for coordinated THT reported in the literature as having medium to strong intensity [86]. A very weak peak at 1023 was observed in this sample as well. No explanation can be offered for this peak other than minor impurity. The far-IR spectrum is dominated by the very strong peak at 388 cm^{-1} which is due to vibrations of the cluster. In all of the derivatives, the Mo-S vibration occurs as a strong peak at 383 to 393 cm^{-1}. The absence of vibrations at 346 and 300 cm^{-1} in the far-IR region confirms the absence of any chloride in the clusters [87].

Table XI. Infrared absorption frequencies (cm^{-1}), of some $Mo_6S_8 \cdot 6L$ compounds

$Mo_6S_8 \cdot npy$	$Mo_6S_8 \cdot (6\text{-}x)PrNH_2$	$Mo_6S_8 \cdot 6THT$	$Mo_6S_8 \cdot 6SEt_2$[a]
Mid-Infrared:			
1601(m)[b]			
	1566(w)		
		1306(ms)	
1260(m)[c]	1261(mw)	1269(m)	1261(ms)
		1254(m)	
1150(w,b)		1130(m)	
			1097(s,b)
1066(mw)		1070(ms)	
1036(mw)	1032(m,b)	1035(vw)	
1020(vw,b)		1023(vw)	
	997(mw)		
		957(m)	
		879(ms)	
	860(mw)		
800(m,b)	804(m,b)	808(m)	802(s)
752(mw)	750(mw)		
692(m)			
		673(w)	
		665(vw)	
Far-infrared:			
631(mw)			
		515(m)	
			476(m,b)
		466(w,b)	
393(m,vb)	384(s,b)	388(vs)	383(m,b)
		279(w)	
		272(m)	

[a]Due to very low yield, the mull was not very concentrated and therefore the intensities were not as strong as expected.

[b]Relative intensities are given in parentheses: s=strong, m=medium, w=weak, b=broad.

[c]These bands are most likely due to the presence of silicone stopcock grease in the samples.

CONCLUSIONS

It appears from the work here that the *n*-propylamine derivative of $Mo_6S_8 \cdot 6L$ is more reactive toward ligand replacement by sulfur donors than the pyridine derivative. This may be due to the absence of intercluster interactions in the *n*-propylamine derivative. Thioether derivatives are not as easily prepared as the well characterized triethylphosphine derivative. Only the tetrahydrothiophene derivative was isolated in practical yields.

The crystal structure was solved for $Mo_6S_8 \cdot 6THT$. The cluster has nearly ideal octahedral symmetry. The Mo-Mo bond lengths are slightly shorter than found in $Mo_6S_8 \cdot 6PEt_3$, but limited evidence is available to establish the reason for this.

GENERAL SUMMARY

The reactivity of bridging ligands in Mo_6 cluster containing compounds, specifically Mo_6Cl_{12}, was exploited in this work to prepare mixed sulfide chloride clusters, $Mo_6Cl_{(8-x)}S_x$. Because of the potential use of the molecular compounds as precursors to Chevrel phase compounds, the properties of the molecular compounds must be better understood. Steps were made toward such understanding.

Because of previous problems in isolating pure compounds with mixed bridging ligands, purification of these mixtures was a goal of this research. The reaction of Mo_6Cl_{12} with sodium hydrosulfide in the presence of a stoichiometric amount of sodium butoxide produced a mixture of sulfided clusters. When the reaction stoichiometry was four equivalents of sodium hydrosulfide, a cluster product was produced which had an average composition of approximately $[Mo_6S_{3.6}Cl_{4.8}]\cdot 4py$. After derivitization and chromatographic separation, compounds with the cluster compositions $[Mo_6S_8]$, $[Mo_6S_{\sim 5}Cl_{\sim 3}]$, and $[Mo_6S_4Cl_4]$ were isolated as the triethylphosphine derivatives, $Mo_6Cl_{(8-x)}S_x\cdot 6PEt_3$, or the triethylphosphine oxide derivative as was the case when x = 4.

Separations on a basic alumina column were achieved based on chlorine content of the compound. The interaction between aluminum and chlorine seems to be the retention mechanism because the cluster containing no chlorine did not adsorb to the column at all and subsequently eluted fractions contained increasingly more chlorine.

The substitution of ligands in the terminal positions of the $Mo_6S_8 \cdot 6L$ cluster was found to depend upon both the substituting ligand and the reactant cluster's leaving ligand. Tetrahydrothiophene (THT), was the most reactive of the three thioethers tried at replacing the ligands of $Mo_6S_8 \cdot npy$ or $Mo_6S_8 \cdot (6\text{-}x)PrNH_2$. Also, *n*-propylamine ligands seemed more readily replaced than pyridine ligands. When the $PrNH_2$ derivative was reacted with THT, crystalline material was obtained.

Substitution of outer ligands in complexes of Mo_6 has been studied to a great extent. In addition to the substitution chemistry discussed above, the removal of the terminal ligands was examined as a method of preparing the Chevrel phases at lower temperatures. The transfer of the ligands of $Mo_6S_8 \cdot 6PEt_3$ to other complexes was examined. Reaction of $Mo_6S_8 \cdot 6PEt_3$ with molybdenum hexacarbonyl or dicobalt octacarbonyl resulted in low yields of insoluble products. The insolubility and weak absorptions in the infrared spectra did suggest that the products were partially de-ligated, that is, they had less than six triethylphosphine ligands remaining.

When $Mo_6S_8 \cdot 6PEt_3$ was reacted with copper(I) chloride in refluxing toluene, 100% of the product was insoluble. Unfortunately, the product contained CuCl in some form. Some triethylphosphine also remained but it could not be determined whether it was bound to the copper or the cluster.

Finally, chemical transformation of the ligand to the non-coordinating species triethylphosphine sulfide was attempted. In this reaction, approximately 20% of the product was insoluble. This product's infrared spectrum showed only weak peaks associated with coordinated triethylphosphine. Also, triethylphosphine sulfide was isolated from the soluble product and identified by its infrared spectra. These results

suggested that the reaction proceeded as predicted. However, the elemental analysis of the product indicated that it contained triethylphosphine sulfide in some form. Triethylphosphine sulfide was recovered by reacting this product with triethylphosphine, which supports the existence of triethylphosphine sulfide coordinated to the cluster. However, that is not supported by the infrared spectrum where no peak for the P=S stretch was observed, either as the free ligand or coordinated ligand.

FUTURE WORK

Research in the area of compounds with hexanuclear molybdenum clusters has been going on for quite some time. The structures and properties of molybdenum(II) halides were studied in the 1960s. The discovery of superconducting Chevrel phases spurred a great deal of research on these compounds during the 1970s. Throughout the 1980s, new solid state compounds with the hexanuclear clusters were prepared and characterized.

In this research, as well as previous work in this group, the sulfidation of molecular clusters was studied. Much progress was made toward the isolation of mixed chloride sulfide clusters. Many of the mixed ligand species can now be prepared and purified. Microcrystalline material has been prepared but further efforts to grow single crystals suitable for x-ray diffraction studies are needed to study the trends of the entire series, $[Mo_6Cl_{(8-x)}S_x]$.

Further purification of the clusters $Mo_6Cl_{(8-x)}S_x \cdot 6PEt_3$, where $5 \leq x \leq 7$, is needed before their structures can be solved with confidence. Structural data for these clusters will answer questions about the effect of oxidation state on Mo-Mo bond lengths. Also interesting will be the electronic properties of the clusters with $5 \leq x \leq 7$. The clusters with $x = 5$ and $x = 7$ will surely be paramagnetic. The $x = 6$ species may or may not be paramagnetic and a Jahn-Teller distortion is predicted. The use of electron paramagnetic resonance spectroscopy has been very limited and more detailed studies need to be done. Cyclic voltammetry would further elucidate

the eletrochemical properties of mixed chloride sulfide species with 20 to 24 electrons per cluster.

The de-ligation of $Mo_6S_8 \cdot 6PEt_3$ has not been shown here to proceed easily to the binary Mo_6S_8. The use of triethylphosphine ligand in the preparation of the molecular cluster was to assure complete ligation and solubility. Its strength as a coordinating ligand assured the desirable properties in studying the molecular species, but for the same reasons, prevented its removal to give a Chevrel phase material. Better choices for ligands might be aryl substituted phosphines which tend to be weaker coordinators, or amines. There is evidence that *n*-propylamine is removed from the cluster, at least to give a $Mo_6S_8 \cdot 4PrNH_2$ species, under vacuum at room temperature [15]. The lability of this ligand may make $Mo_6S_8 \cdot (6\text{-}x)PrNH_2$ a more feasible candidate as a precursor to Mo_6S_8. An appropriate precursor must be soluble and its ligands must be fairly labile. Further study on the substitution of ligands of the $Mo_6S_8 \cdot 6L$ cluster compounds is required before further work on de-ligation is continued.

Further, it may be useful to undertake a study of a controlled de-ligation. That is, try to remove only one or two ligands per cluster at a time. If compounds with four or five ligands can be characterized, the information may be useful in developing methods for the complete de-ligation. Also, such partially ligated species may themselves have interesting structures and provide insight into the nature of the intercluster bonding found in the Chevrel phases.

Some substitution reactions were done in this work toward the goal of preparing thioether derivatives. Additional substitutions have been studied [15]. It

seems that propylamine easily replaces pyridine and disrupts the intercluster linkages formed during the preparation of the sulfided cluster. Further, the propylamine ligand is quite labile and is removed under vacuum at room temperature. It was found here that the propylamine cluster derivative was more reactive toward substitution by thioether ligands than the pyridine derivative. Continued investigations may provide useful information about which derivatives may best be used as precursors to Chevrel phase compounds.

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APPENDIX

Table XII. Anisotropic temperature factors (Å^2, x10^2), for the heavy atoms of $Mo_6S_8 \cdot 6THT$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	37 (2)	39 (2)	39 (2)	3 (2)	6 (1)	1 (2)
S(1)	48 (5)	57 (6)	33 (4)	-9 (4)	-4 (4)	1 (4)
S(2)	46 (4)	46 (4)	46 (4)	2 (4)	2 (4)	2 (4)
S(3)	85 (7)	54 (7)	55 (6)	-15 (5)	-25 (5)	2 (4)

Table XIII. Calculated fractional atomic coordinates (x 10^4), for the hydrogen atoms of $Mo_6S_8 \cdot 6THT$

Atom	x	y	z	U
H1a	4557.3	5792.3	2145.9	50.7
H1b	5077.0	5967.6	2839.8	50.7
H2a	4383.5	6779.7	2029.8	50.7
H2b	4896.7	6954.4	2728.6	50.7
H3a	3596.2	7072.3	2526.3	50.7
H3b	4112.3	7267.8	3217.5	50.7
H4a	3069.1	6355.5	3131.8	50.7
H4b	3600.9	6533.1	3815.8	50.7

Table XIV. Non-essential bond distances (Å), and angles (deg), in $Mo_6S_8 \cdot 6THT$

Distances		Angles	
S(3)-C(1)	1.75 (5)	C(1)-S(3)-C(4)	91. (3)
S(3)-C(4)	1.77 (5)	S(3)-C(1)-C(2)	115. (4)
C(1)-C(2)	1.34 (8)	C(1)-C(2)-C(3)	111. (5)
C(2)-C(3)	1.26 (9)	C(2)-C(3)-C(4)	120. (5)
C(3)-C(4)	1.52 (8)	C(3)-C(4)-S(3)	102. (4)

Table XV. Structure factor table for $Mo_6S_8 \cdot 6THT$. The H index will serve as column headings. Its maximum value is 20 and its minimum value is 0. Number of pieces of data = 227. Multiplicative scale factor for Fo & Fc = 1.000. The Fc will be signed

H = 2

K	L	Fo	Fc
0	0	946	875
1	1	60	-50
2	0	535	537
2	2	390	383
4	0	135	122
5	1	96	77
7	1	103	74
8	0	139	-148
18	0	187	-187
20	0	129	-136

H = 3

K	L	Fo	Fc
2	1	176	176
3	2	191	-184
7	2	132	138
9	2	266	258
10	1	91	-76
11	2	129	143
14	1	120	97
16	1	135	125
18	1	165	153
20	1	113	71

H = 4

K	L	Fo	Fc
1	1	160	-156
2	0	200	197
3	3	131	-131
4	2	140	-140
4	4	248	-243
5	1	106	97
8	0	112	117
9	3	149	-155
10	0	103	106
12	2	111	106
14	2	123	125
15	3	127	119
17	3	123	116
18	0	144	-139
18	2	120	-109
20	0	120	-109
20	2	115	-100

H = 5

K	L	Fo	Fc
2	1	95	82
5	2	155	-162
5	4	106	-120
6	3	148	-148
7	4	91	-77
8	3	177	-180
9	2	90	53
10	3	127	-119
11	2	104	110
12	1	189	190
13	2	115	92
14	1	191	195
14	3	117	98
16	1	175	174
16	3	119	109
18	1	128	116

H = 6

K	L	Fo	Fc
0	0	190	-203
1	1	107	89
2	0	278	-262
2	2	103	-84
3	3	214	-220
4	0	323	-323
4	2	187	-199
5	3	204	-216
5	5	276	-274
6	2	107	-116
7	1	91	-90
7	3	179	-174
7	5	235	-243
8	0	205	204
9	5	104	-100
10	0	104	105
10	2	105	90
10	4	137	135
11	3	133	138
12	0	106	111
12	2	157	153
12	4	169	173
13	1	104	77
13	3	136	131
14	0	172	169
14	2	179	173
14	4	115	113
15	1	115	96
15	3	134	125
16	2	112	97

H = 7

K	L	Fo	Fc
2	1	185	183
4	1	297	314
4	3	164	173
5	2	172	-179
5	4	208	-219
6	1	282	294
6	3	97	92
6	5	187	-199
7	4	127	-127
7	6	160	-164
8	1	110	107
8	5	118	-119
9	4	105	-92
10	3	113	-109
12	1	115	98
14	1	144	141
16	1	137	125

H = 8

K	L	Fo	Fc
0	0	337	-328
2	0	175	-181
2	2	103	-114
3	3	244	-235
4	0	207	-211
4	2	110	-131
5	1	120	-112
5	3	325	-317
5	5	263	-268
6	0	116	-120
7	1	107	-111
7	3	138	-145
7	5	149	-154
7	7	114	-116
10	0	101	-88
10	4	108	105
11	3	165	170
11	5	154	155
11	7	116	109
13	1	116	107
13	3	200	205
13	5	184	190
13	7	137	137
14	0	185	191
14	2	151	144
15	3	139	137
15	5	132	130
16	0	116	113
19	7	108	-75

H = 9

K	L	Fo	Fc
2	1	401	399
4	1	563	554
4	3	396	390
5	4	214	-211
6	1	290	302
6	3	275	287

Table XV (continued).

6	5	94	75
7	4	112	-109
7	6	114	-94
11	4	109	-68
12	7	126	-114
14	7	137	-141

H = 10

K	L	Fo	Fc
0	0	153	-152
2	0	175	-175
2	2	112	-108
3	3	107	-106
4	0	197	-198
4	2	104	-105
4	4	95	110
5	3	216	-226
5	5	146	-151
6	0	175	-192
6	4	132	141
7	3	115	-128
11	3	112	90
11	5	152	148
11	7	159	161
11	9	129	128
13	3	191	196
13	5	231	226
13	7	146	146
15	3	125	121
15	5	136	148

H = 11

K	L	Fo	Fc
2	1	198	191
4	1	356	350
4	3	171	176
5	2	108	-100
5	4	132	-138
6	1	202	207
6	3	135	142
7	4	117	-127
10	9	115	102
11	10	115	101

H = 12

K	L	Fo	Fc
2	0	114	-99
4	0	104	-97
4	4	144	143
5	3	179	-183
5	5	115	-114
6	4	121	115
6	6	115	116
7	3	109	-103
11	5	114	97
12	4	120	-102
12	6	115	-97
12	12	125	125
13	5	126	130
14	6	118	-112
16	6	108	-92

H = 13

K	L	Fo	Fc
8	1	116	-116
10	1	118	-103
10	9	112	102
11	4	123	-108
13	2	124	-117
13	4	123	-129

H = 14

K	L	Fo	Fc
4	4	111	90
6	0	114	85
10	0	115	-107
10	2	117	-122
10	4	123	-113
11	3	116	-107
12	0	109	-111
12	2	116	-121
12	4	129	-133

H = 15

K	L	Fo	Fc
6	1	137	-145
7	2	117	-115
8	1	183	-186
8	3	121	-125
10	1	145	-152
11	4	127	-131

H = 16

K	L	Fo	Fc
3	3	120	99
6	0	126	106
12	2	111	-73

H = 17

K	L	Fo	Fc
4	1	124	-111
6	1	118	-100
8	1	131	-123
9	2	117	-76
9	4	122	-96
10	1	141	-134

H = 18

K	L	Fo	Fc
0	0	176	-177
1	1	120	98
2	0	142	-148
2	2	153	-149
6	0	154	156
8	0	138	141
8	2	122	110

H = 20

K	L	Fo	Fc
0	0	123	-100
2	2	109	-93
6	0	118	99